Technical Report SERDP-98-7
March 1998

US Army Corps of Engineers
Waterways Experiment Station

Strategic Environmental Research and Development Program

A Pilot-Scale Assessment of Peroxone Oxidation for Potential Treatment of Three Contaminated Groundwaters at the Rocky Mountain Arsenal, Commerce City, Colorado

by Mark E. Zappi, Elizabeth C. Fleming, Todd Miller, Fred Ragan, Randy Swindle, Robert Morgan, Steven Harvey

Prepared for Headquarters, U.S. Army Corps of Engineers
and Office of Program Manager, Rocky Mountain Arsenal

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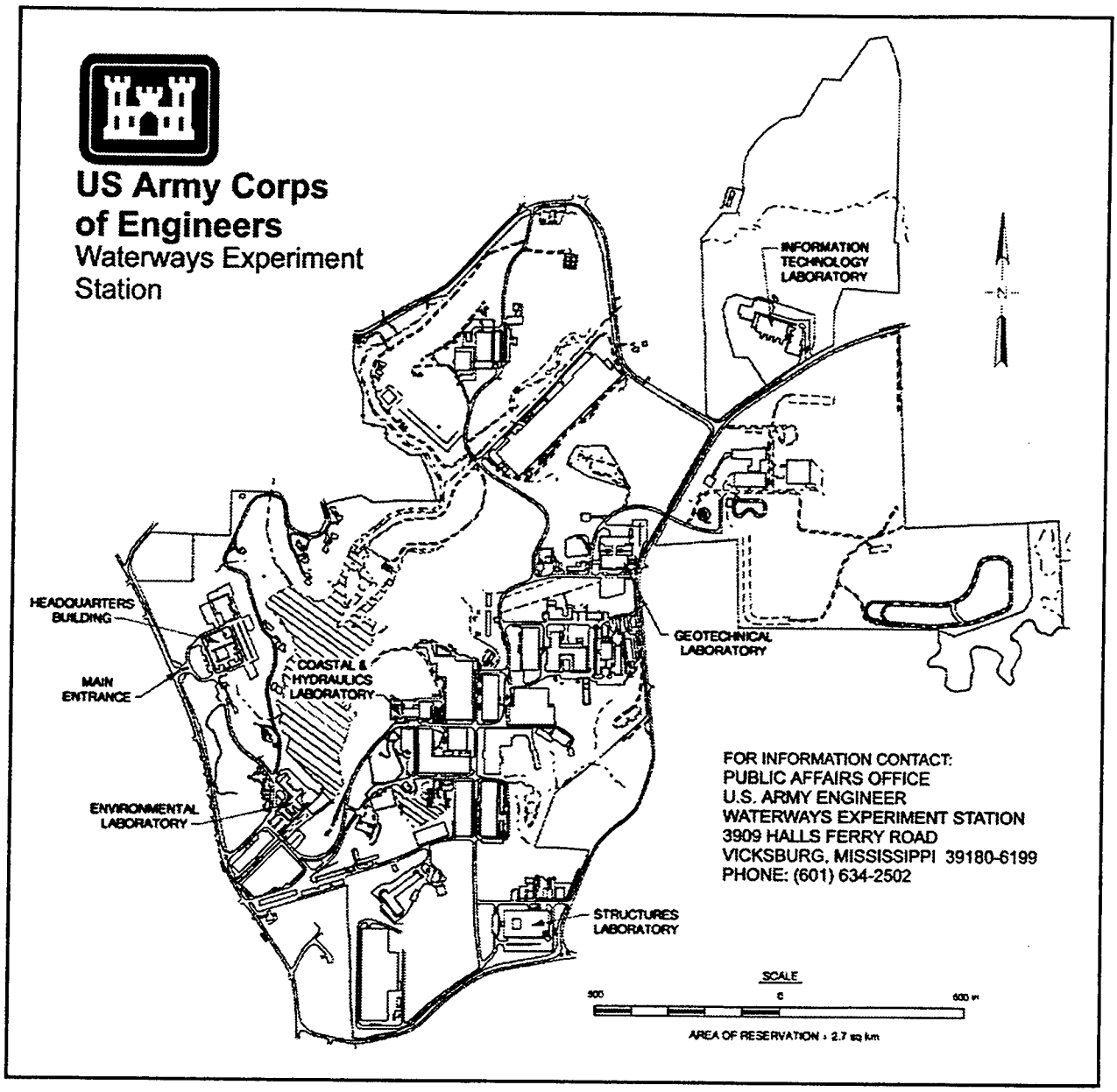
Final report

Prepared for U.S. Army Corps of Engineers
Washington, DC 20314-1000
and Office of Program Manager, Rocky Mountain Arsenal
Commerce City, CO 80022-2180



Waterways Experiment Station Cataloging-in-Publication Data

A pilot-scale assessment of peroxone oxidation for potential treatment of three contaminated groundwaters at the Rocky Mountain Arsenal, Commerce City, Colorado / by Mark E. Zappi ... [et al.] ; prepared for U.S. Army Corps of Engineers and Office of Program Manager, Rocky Mountain Arsenal.

87 p. : ill. ; 28 cm. -- (Technical report ; SERDP-98-7)

Includes bibliographic references.

1. Hydrogen peroxide -- Testing. 2. Pesticides -- Environmental aspects. 3. Groundwater -- Purification. 4. Groundwater -- Contamination. I. Zappi, Mark E. II. United States. Army. Corps of Engineers. III. U.S. Army Engineer Waterways Experiment Station. IV. Strategic Environmental Research and Development Program (U.S.) V. Program Manager for Rocky Mountain Arsenal (Colo.) VI. Series: Technical report (U.S. Army Engineer Waterways Experiment Station) ; SERDP-98-7.

TA7 W34 no.SERDP-98-7

Contents

List of Figures

List of Tables

Preface

The work described herein was performed as a partnering effort between the Office of Program Manager, Rocky Mountain Arsenal (PMRMA), Commerce City, CO, and the U.S. Army Engineer Waterways Experiment Station (WES), Vicksburg, MS. Funding for performance of this effort was provided to WES by PMRMA and the U.S. Department of Defense's Strategic Environmental Research and Development Program (SERDP).

This report was prepared by Dr. Mark E. Zappi, Ms. Elizabeth C. Fleming, Messrs. Todd Miller, Fred Ragan, and Randy Swindle, CAPT Robert Morgan, and MAJ Steven Harvey, Environmental Restoration Branch (ERB), Environmental Engineering Division (EED), Environmental Laboratory (EL), WES. Significant contributions were made to this project by Mr. Elijah Jones, Analytical Laboratory, PMRMA; Messrs. Tom James, Robert Stalworth, David Strang, and James Smith, EED, PMRMA; Messrs. Sidney Ragsdale, Richard Karn, and Norman Francingues, EED, WES; Ms. Danea Guimbellot, ERB, WES; Ms. Ann Strong, Chief, Environmental Chemistry Branch, EED, WES; Mr. John Mahoney, Directorate of Public Works, WES; and Dr. Ellen Kaastrup, Foster Wheeler Environmental Corporation, Lakewood, CO.

This project was performed under the direct supervision of Mr. Daniel Averett, Chief, ERB, WES, and Mr. Brian Anderson, PMRMA, and the general supervision of Mr. Norman Francingues, Chief, EED, WES; Dr. John Harrison, Director, EL, WES; and Mr. Charlie Scharmann, Chief, EED, PMRMA.

Dr. M. John Cullinane, EL, was the WES Program Manager for the SERDP. Dr. John Harrison was the Director of SERDP at the time of this project.

At the time of publication of this report, Dr. Robert W. Whalin was Director of WES, and COL Robin R. Cababa, EN, was Commander. Mr. Kevin Blose was the Technical Director for Rocky Mountain Arsenal, and COL Eugene Bishop, EN, was the Program Manager.

This report should be cited as follows:

Zappi, M. E., Fleming, E. C., Miller, T., Ragan, F., Swindle, R., Morgan, R., and Harvey, S. (1998). "A pilot-scale assessment of peroxone oxidation for potential treatment of three contaminated groundwaters at the Rocky Mountain Arsenal, Commerce City, Colorado," Technical Report SERDP-98-7, U.S. Army Engineer Waterways Experiment Station, Vicksburg, MS.

Conversion Factors, Non-SI to SI Units of Measurement

Non-SI units of measurement used in this report can be converted to SI units as follows:

Multiply	By	To Obtain
acres	4,046.873	square meters
feet	0.3048	meter
gallons (U.S. liquid)	3.785412	liters
inches	2.54	centimeters

1 Introduction

Rocky Mountain Arsenal (RMA) is a U.S. Army installation that occupies more than 17,000 acres[1] in Adams County, Colorado. RMA was established in 1942 and has been the site of chemical incendiary munitions manufacturing and chemical munitions demilitarization. Following World War II, Congress approved the leasing of some portions of RMA to private industry. Agricultural pesticides and herbicides were manufactured onsite from 1947 to 1982. Past military and industrial activities at RMA have resulted in the contamination of the alluvial aquifer with various organic compounds such as diisopropylmethylphosphonate (DIMP), pesticides, and volatile organic compounds (VOCs).

In support of the Office of Program Manager, Rocky Mountain Arsenal (PMRMA), the U.S. Army Engineer Waterways Experiment Station (WES) evaluated chemical oxidation processes for treatment of several RMA contaminated groundwaters using bench-scale reactors (Zappi et al., in preparation). One conclusion drawn from these efforts was the potential use of peroxone oxidation for treatment of several RMA groundwaters. Due to the innovative and developmental nature of peroxone for groundwater treatment, pilot studies were required to fully evaluate the feasibility of peroxone as a potential treatment option at RMA.

This report describes the results of three pilot studies performed at RMA during August 1994 that were designed to evaluate the potential uses of peroxone oxidation at RMA. Peroxone was evaluated using a mobile pilot-scale peroxone system with a flow capacity of 0.5 to 10 gpm designed and constructed by WES. Three groundwaters, considered chemically characteristic of the range of RMA waters that are being treated or may require treatment in the future, were treated using the peroxone pilot unit. The results of this effort will be used by RMA to evaluate potential applicability of peroxone toward RMA contaminants and the various respective levels of those contaminants within differing geochemical matrices. This approach should provide a technically sound basis to evaluate the applicability of peroxone at the RMA.

[1] A table of factors for converting non-SI units of measurement to SI units is presented on page viii.

Study Scope

This effort was approached as a partnering effort between RMA and WES. The RMA was interested in the potential of the peroxone unit to treat various contaminated groundwaters at the Arsenal. WES, while interested in the capabilities of peroxone at RMA, used these studies to assess the adequacy of the peroxone pilot system design as a mobile pilot-scale system for performance of groundwater treatability assessments.

WES has been tasked by the Department of Defense's (DoD) Office of Strategic Environmental Research Development Program to investigate the potential of peroxone for treating explosives-contaminated groundwaters at DoD installations. The results of these pilot studies were used by WES to identify design flaws and optimize system performance (system shake-down). WES intends to use the pilot unit for future studies at several other military installations for evaluating peroxone for potential treatment of contaminated groundwaters.

Chemical Oxidation

Chemical oxidation is a group of treatment technologies that use powerful chemical oxidizers to destroy organic contaminants. Typical oxidizers used in chemical oxidation processes include ozone (O_3), chlorine, hydrogen peroxide (H_2O_2), and potassium permanganate. The chemical reaction products are usually simple organic compounds, such as carboxylic acids, and/or inorganic compounds, such as carbon dioxide, water, and chlorides, which are caused by the oxidation of chlorinated solvents.

The peroxone technology has historically been used as a treatment technology for municipal drinking water (Metcalf and Eddy, Inc. 1991). Chlorination has been used almost exclusively in the United States for disinfection of municipal drinking water (James Montgomery Engineers, Inc. 1985). Chemical oxidation has been used primarily in conjunction with ultraviolet (UV) photolysis for contaminated site remediation and industrial wastewater treatment. Hydrogen peroxide (H_2O_2) and ozone (O_3) have been used almost exclusively in conjunction with UV photolysis with respect to groundwater remediation projects. Mayer et al. (1990) concluded that chemical oxidation processes are very competitive with both air stripping and activated carbon adsorption for treating VOCs in contaminated groundwaters.

Chemical oxidation processes that result in the generation of the hydroxyl radical ($OH^{\cdot}$) have been referred to as advanced oxidation processes (AOPs) by the American Water Works Association (1991). Commercial application of AOPs for contaminated groundwater treatment in the United States has traditionally involved UV irradiation of H_2O_2, O_3, or a combination of both. In UV light-based AOPs, irradiation of chemical oxidizers with UV light produces hydroxyl radicals. The hydroxyl radical is a much more powerful oxidizer than either H_2O_2 or O_3 (Sundstrom et al. 1986).

Zappi et al. (1990) evaluated a UV/hydrogen peroxide system for treatment of three contaminated waters at the RMA. The waters investigated were the influent to the North Boundary System, a hydrazine wastewater, and South Plants groundwater (contained high levels of benzene (approximately 400 mg/ℓ)). Their results indicated DIMP was easily removed from the North Boundary waters via oxidation; hydrazine-based contaminants were removed from the wastewater; and the benzene levels were too high for the treatment times evaluated (i.e., 20 min). The positive results of Zappi et al. (1990) were the genesis of the present study, because the 1990 results indicated that many RMA contaminants were amenable to degradation via oxidation to within target treatment goals.

Peroxone

Peroxone is an AOP that uses the combination of H_2O_2 and O_3 to form the hydroxyl radical without the requirement of UV light. Since photolysis is not required for producing hydroxyl radicals via peroxone reactions, then it can be said that peroxone is a "dark" AOP.

The results reported by Glaze and Kang (1988) indicated that peroxone could effectively degrade chlorinated solvents from the groundwater. Since peroxone does not require the addition of high concentrations of chemical oxidizers and UV light, it is estimated that reductions in treatment costs as high as 90 percent may be realized.

Langlais, Reckhow, and Brink (1991) present the following mechanism for the formation of the hydroxyl radical during peroxone treatment:

$$H_2O_2 + H_2O \;<\!-\!-\!>\; HO_2^- + H_3O^+ \qquad (1)$$

$$O_3 + HO_2^- \;-\!-\!>\; OH + O_2^- + O_2 \qquad (2)$$

$$O_2^- + H^+ \;<\!-\!-\!>\; HO_2 \qquad (3)$$

$$O_3 + O_2^- \;-\!-\!>\; O_3^- + O_2 \qquad (4)$$

$$O_3^- + H^+ \;<\!-\!-\!>\; HO_3 \qquad (5)$$

$$HO_3 \;-\!-\!>\; OH\cdot + O_2 \qquad (6)$$

Discussions with French researchers indicate that some water utilities in France are currently using peroxone to treat millions of gallons per day of pesticide-contaminated groundwater.[1] The French researchers claim that treatment costs are $0.05 per 1,000 gal.

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[1] Personal Communication, 1992, Dr. Marcel Dore, University of Poitiers, France.

Glaze and Kang (1988) performed laboratory-scale studies on the ability of peroxone to remove trichloroethylene (TCE) and tetrachloroethylene (PCE) from a contaminated groundwater. The results proved positive enough to warrant subsequent pilot-scale evaluations (Aieta et al. 1988). Both the bench and pilot studies concluded that the reaction rate of TCE and PCE was increased by factors of 1.8 to 2.8 and 2.0 to 6.5, respectively, as opposed to those achieved by ozonation alone. Apparently, TCE was reactive toward ozone alone as well as the hydroxyl radicals formed; PCE was only reactive toward the radical species. Both studies indicated that a hydrogen peroxide-to-ozone ratio between 0.25 and 0.50 was optimal for removing TCE and PCE from the groundwater studied.

The Metropolitan Water District of Southern California (1991) evaluated peroxone using pilot-scale systems for treatment of 2-methyllisoborneal (MIB) and trans-1,10-dimethyl-trans-9-decanol (geosmin). The District concluded that optimum hydrogen peroxide-to-ozone ratios for removal of MIB and geosmin was 0.1 to 0.2. It further concluded that peroxone was better for removal of MIB and geosmin than ozone alone due to increased hydroxyl radical production.

Zappi (1995) evaluated peroxone as a means of removing 2,4,6-trinitrotoluene (TNT) from aqueous solutions. His results indicated that a 100-mg/ℓ hydrogen peroxide batch added to an ozonated reactor (continuously sparged with 2-percent ozonated air) was the optimal system evaluated for removing TNT and related by-products. In fact, his research indicated that small or large additions of hydrogen peroxide added to the same system had an adverse impact on TNT removal rates. These observations exemplify the scavenging effect of excess dosing of the parent oxidizers on the removal of contaminants from waste streams. This is discussed in much greater detail in Chapter 2 of this report.

Study Objectives

The objective of this study was to evaluate the technical feasibility of using peroxone systems for treatment of contaminated groundwaters at the RMA using a pilot-scale peroxone system. Feasibility was evaluated as the level of treatment afforded by the various candidate oxidizer dosages and hydraulic residence times (HRTs). The targeted treatment goals for this study by WES was below detection levels (BDLs).

A secondary objective of WES was to evaluate the pilot system design and develop standard operating protocols for future testing at other DoD installations containing groundwaters contaminated with organic contaminants. This allowed for identification of design flaws and provided information of further process optimization.

Three RMA groundwater influents were used for evaluating process feasibility. These groundwaters were selected because they represented uniquely different groundwater geochemical matrices that were considered characteristic to potential RMA influents. The groundwater sources are listed below:

a. Influent to the North Boundary Containment System (NBCS).

b. Composite of Basin A/South Plants Groundwaters.

c. Basin A Neck System (BANS) Groundwater.

Well numbers and relative chemical characteristics and pilot system operation will be discussed in Chapters 2 and 3 of this report.

2 Radical Formation in Peroxone Systems

The reactions between H_2O_2 and O_3 that result in the formation of the hydroxyl radical have been under investigation since the early 1950s when Taube and Bray (1940) first described potential radical formation reactions. The hydrogen peroxide-ozone reactions were later defined by the engineering community as peroxone. A thorough literature review was undertaken at WES as an attempt to quantify and qualify key mechanistic reactions that result in the formation of hydroxyl radicals during AOP treatment. This effort was used to present the following information detailing hydroxyl radical formation mechanisms and related radical scavenging reactions.

Figure 1 presents a mechanistic diagram that details hydroxyl radical fate during AOP treatments that use both H_2O_2 and O_3. Radical production mechanisms illustrated in Figure 1 include UV photolysis, peroxone, and hydroxide ion-based ozone decomposition. Hydroxyl radical sinks or scavenging mechanisms (Note: scavengers other than the contaminant are represented as "S_i" in Figure 1) include reactions with ozone, hydrogen peroxide, contaminants (illustrated as Species A), and/or common water constituents such as carbonate and cationic species. From these series of reactions including initiation, propagation, and termination reactions, a steady-state hydroxyl radical concentration is developed. Mechanisms can be grouped into two types: dark and illuminated. Since peroxone involves only dark reactions, then only the dark mechanisms are discussed.

Dark Ozone Reactions

It is widely known that ozone reacts with the hydroxide ion at high pHs to decompose ozone (Staehelin, Buhler, and Hoigne 1984). As illustrated in Figure 1, ozone reacts readily with the hydroxide ion at high pH to produce superoxide ($HO_2\cdot$ and $O_2\cdot^-$) and/or peroxide (HO_2^-) (Bahnemann and Hart 1982). The stoichiometric mechanisms responsible for superoxide and peroxide production due to alkalinity are presented below:

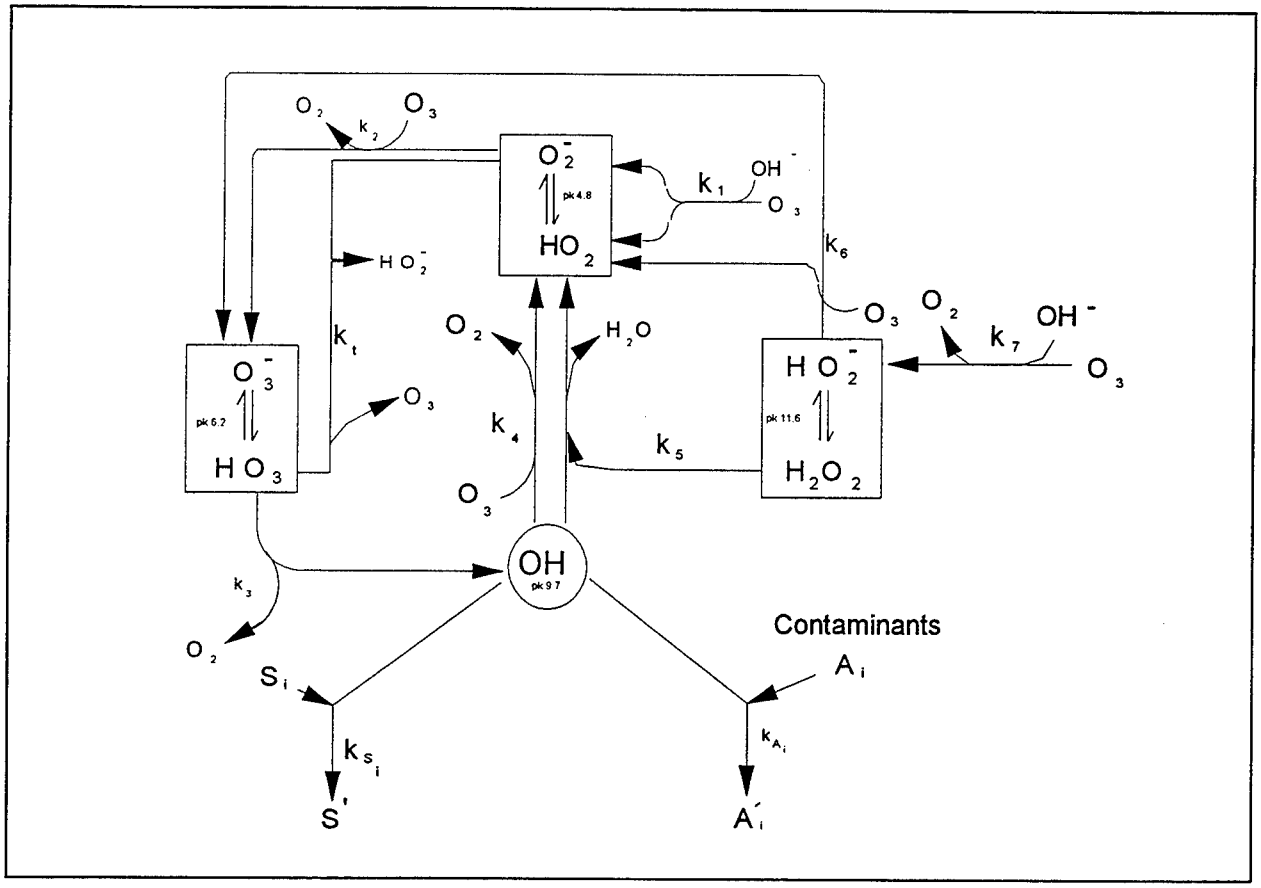

Figure 1. Hydroxyl radical formation/scavenging mechanisms during AOP treatment (Hong, Zappi, and Kuo 1954)

$$O_3 + OH^- \rightarrow O_2^{\cdot -} + HO_2^{\cdot} \qquad k_1 = 70\ M^{-1}s^{-1} \tag{7}$$

$$O_3 + OH^- \rightarrow HO_2^- + O_2 \qquad k_7 = 48\ M^{-1}s^{-1} \tag{8}$$

The latter product further reacts with ozone to form a hydroxyperoxide ($HO_2^{\cdot}$) and an ozonide ion ($O_3^{\cdot -}$) as described by Staehelin and Hoigne (1982):

$$HO_2^- + O_3 \rightarrow HO_2^{\cdot} + O_3^{\cdot -} \qquad k_6 = 2.8 \times 10^6\ M^{-1}s^{-1} \tag{9}$$

Once superoxide ions ($O_2^{\cdot -}$) are formed, then they react with ozone to produce an ozonide, $O_3^{\cdot -}$. The ozonide ion then releases an oxygen to produce the hydroxyl radical as illustrated below (Staehelin, Buhler, and Hoigne 1984):

$$O_2^{\cdot -} + O_3 \rightarrow O_3^{\cdot -} + O_2 \qquad k_2 = 1.6 \times 10^9\ M^- \tag{10}$$

$$HO_3^{\cdot} \rightleftharpoons H^+ + O_3^{\cdot -} \qquad pK_a = 6.2 \tag{11}$$

$$HO_3^{\cdot} \rightarrow \cdot OH + O_2 \qquad k_3 = 1.1 \times 10^5\ s^{-1} \tag{12}$$

As previously stated, the radical is a very powerful oxidant, and once it is formed, it will attack and oxidize most organic compounds (for example, Contaminant A). Unfortunately, the hydroxyl radical is not very selective in terms of reactants. Radicals will also react with nonregulated compounds referred to as scavengers (Staehelin and Hoigne 1982). Examples of scavenger species (S) include bicarbonates (HCO_3^-) and carbonates (CO_3^{2-}). Key hydroxyl radical reactions are summarized below:

a. Reaction with a regulated contaminant Contaminant A (i.e., DIMP):

$$\cdot OH + A_i \rightarrow A_i' + OH^- \qquad k_{Ai} = 1^{st} \text{ order rate constant} \tag{13}$$

b. Reactions with scavengers (S (i.e., bicarbonates and carbonates)):

$$\cdot OH + HCO_3^- \rightarrow HCO_3^{\cdot} + OH^- \qquad k_{s1} = 1.5 \times 10^7 M^{-1}s^{-1} \tag{14}$$

$$\cdot OH + CO_3^{2-} \rightarrow CO_3^{\cdot -} + OH^- \qquad k_{s2} = 4.2 \times 10^8 M^{-1}s^{-1} \tag{15}$$

The hydroxyl radical may also be converted to superoxide ($HO_2\cdot$) by reacting with ozone (Sehested et al. 1984), hydrogen peroxide (Christensen, Sehested, and Corfitzen 1982), or a chain promotor (P_i) such as t-butyl alcohol, which is referred to as a tertiary alcohol (Staehelin and Hoigne 1982). It should be noted that t-butyl alcohol was used by Zappi (1995) to segregate ozonation and/or hydrogen peroxide reactions from radical-based reactions during treatment of TNT-contaminated waters. His results indicated that TNT removal during peroxone oxidation was indeed hydroxyl radical-based and not due to primary oxidation. Mechanisms of the above-discussed hydroxyl radical scavenging reactions are listed below:

$$\cdot OH + O_3 \rightarrow HO_2^{\cdot} + O_2 \qquad k_4 = 1.1 \times 10^8\ M^{-1}s^{-1} \tag{16}$$

$$\cdot OH + H_2O_2 \rightarrow HO_2^{\cdot} + H_2O \qquad K_5 = 2.7 \times 10^7 M^{-1}s^{-1} \tag{17}$$

$$\cdot OH + P_i \rightarrow R_i^{\cdot} \rightarrow R_iOO\cdot \rightarrow P_i' + HO_2^{\cdot} \qquad k_{pi} \text{ is variable} \tag{18}$$

where k_{pi} is variable and is based on the alcohol species selected.

It has been suggested that the intermediate, $HO_4\cdot$, may also form during the k_4 step listed above (Staehelin, Buhler, and Hoigne 1984). The proposed reactions are presented below:

$$\cdot OH + O_3 \rightleftharpoons HO_4^{\cdot} \quad k_f = 2 \times 10^9 M^{-1}s^{-1};\ k_b < 2.8 \times 10^4 M^{-1}s^{-1} \tag{19}$$

$$HO_4^{\cdot} \rightarrow HO_2^{\cdot} + O_2 \quad k = 2.8 \times 10^4 s^{-1} \tag{20}$$

Since $O_2^{\cdot -}$ and $HO_3^{\cdot}$ may accumulate to significant concentrations, they may be involved in the termination of free radicals via the following termination reactions (Staehelin, Buhler, and Hoigne 1984):

$$O_2^{\cdot -} + HO_3^{\cdot} \rightarrow O_3 + HO_2^- \qquad k_t = 10^{10}\ M^{-1}s^{-1} \tag{21}$$

The reaction pathway described above occurs readily during ozonation of an aqueous solution (i.e., when ozone is introduced to water). During peroxone oxidation, the addition of hydrogen peroxide to an ozonated system will facilitate the same pathway but enhance the k_6 step to become the predominant mechanism for radical production. It should be noted that when hydrogen peroxide is added via dosing, the k_7 step that produces HO_2^- likely becomes negligible as the produced amount will be small compared with the added amount.

By comparing kinetic rate coefficients of Reactions 4.1, 4.6, 4.7, it is apparent that when a hydrogen peroxide dose typical of most AOPs is used (10-200 mg/ℓ), the k_6 step becomes more important than the K_1 step or the original k_7 route in the formation of HO_2/O_2^-. For example, for applied ozone and hydrogen peroxide concentrations of $[O_3] = 2 \times 10^{-5}$ M (1 mg/ℓ) and $[H_2O_2] = 1.5 \times 10^{-3}$ M (50 mg/ℓ) at neutral pH (pH = 7):

$$\begin{aligned} k_6\,[O_3]\ [HO_2^-] &= (2.8 \times 10^6)\,(2 \times 10^{-5})\,(1.5 \times 10^{-3})\,(2.5 \times 10^{-5}) \\ &= 2.1 \times 10^{-6}\,Ms^{-1} \end{aligned} \tag{22}$$

$$k_1\,[O_3]1\,[OH^-] = 70\,(2 \times 10^{-5})\,(10^{-7}) = 1.4 \times 10^{-10}\,Ms^{-1} \tag{23}$$

Therefore, the enhancement of the peroxone system over ozone alone in treatment may be due to the faster chain initiation by the k_6 step within peroxone systems. In addition, when large doses of hydrogen peroxide are added with respect to ozone, the scavenging of hydroxyl radicals by the excessive amount of added hydrogen peroxide (k_5 step) may overtake that by ozonation (k_4 step). For example, for applied doses of 1 mg/ℓ soluble ozone and 50 mg/ℓ hydrogen peroxide, the resulting kinetics listed below clearly highlight the scavenging impact of overdosing of oxidizers within AOP systems:

$$k_4[O_3]\,[\cdot OH] = (1.1 \times 10^8)\,(2 \times 10^{-5})\,[\cdot OH] = 2.2 \times 10^3\,[\cdot OH]\,Ms^{-1} \tag{24}$$

$$\begin{aligned} k_5\,[H_2O_2]\ [\cdot OH]11 &= (2.7 \times 10^7)\,(1.5 \times 10^{-3})\,[\cdot OH] \\ &= 4.0 \times 10^4\,[\cdot OH]\,Ms^{-1} \end{aligned} \tag{25}$$

Steady-State Hydroxyl Radical Concentration Model

It is useful for the dark hydroxyl radical fate mechanisms presented in Figure 1 to be incorporated into a model that will estimate the steady-state levels of radicals present in a given AOP system. This model was proposed by Hong, Zappi, and Kuo (1994) for use in comparing $[\cdot OH]_{ss}$ levels in various test peroxone systems under consideration by design engineers. The model as proposed by Hong et al. is presented below:

$$[\cdot OH]_{ss} = \frac{2k_6 [O_3]\ [H_2O_2]_T\ K_{H_2O_2}\ [H^+]^{-1}}{k_4 [O_3] + k_5\ [H_2O_2]_T + k_A [A] + k_S [S]} \tag{26}$$

This equation reveals a complex dependence of $[OH]_{ss}$ on $[O_3]$, $[H_2O_2]_T$, $[A]$, $[S]$, and pH. The degradation rate is expected to increase and then level off as hydrogen peroxide and/or ozone concentrations are increased from very low to high values.

The steady-state expression for $[\cdot OH]_{ss}$ is useful for explaining the complex kinetics often observed in AOPs. It is also useful as a guide in optimizing treatment conditions and selecting an appropriate treatability test matrix based on influent chemistry. For example, the rate of degradation for a Contaminant A under attack by the $\cdot OH$ can be written as:

$$-\frac{d[A]}{dt} = k[\cdot OH]_{ss}[A] = k_p[A] \tag{27}$$

where k_p (s^{-1}) is the pseudo first-order rate constant.

Supply of Oxidizers

The final expression useful for engineering desired operating conditions is design of ozone transfer into peroxone reactors. One approach is that the addition of hydrogen peroxide can be added continuously within the contents of a reactor or in a single batch dose added at the head of the reactor. This study focused primarily on batch dosing at the head of a system because of the relative ease of system design and operation. However, ozone must be continuously sparged into a reactor to maintain a steady-state concentration during treatment due to the limited steady-state concentration of ozone that is added using a 2- to 10-percent ozonated air feed. The difference between the equilibrium concentration of aqueous ozone subject to its vapor pressure in the gas phase and the actual steady-state ozone concentration can be termed ozone deficit (i.e., $[O_3]^* - [O_3]_{ss}$). The rate of supply of a dilute ozone gas, Q_{O3}, (Ls^{-1}) required to maintain a desired $[O_3]_{ss}$ can then be determined according to:

$$Q_{O_3} \frac{P_{in,O_3} - P_{out,O_3}}{RT} = k_L a V_L ([O_3]^* - [O_3]_{ss}) \quad (28)$$

where

Q_{O3} = rate of supply of dilute O_3/air gas mixture, Ls^{-1}

$P_{in,O3}$; $P_{out,O3}$ = partial pressure of O_3 at entrance and exit, respectively, atm (e.g., 1 percent O_3 gas = 10^{-2} atm)

R = universal gas constant, 0.082 ℓ atm deg^{-1} mol^{-1}

T = temperature, K

$k_L a$ = mass transfer coefficient of O_3, s^{-1}

V_L = volume of liquid being treated, ℓ

$[O_3]^*$ = equilibrium concentration of O_3, M

$[O_3]_{ss}$ = desired steady-state concentration of O_3, M

It should be stressed that the derived expression of $[\cdot OH]$ has been based on instantaneous concentrations of H_2O_2 and O_3 (i.e., residual concentrations at the moment) in the system. The actual (or residual) value of $[O_3]_{ss}$ being maintained for a particular Q_{O3} should be monitored, then the Q_{O3} can be adjusted to meet a target $[O_3]_{ss}$ value. Glaze and Kang (1988) reported an increase in pseudo-first-order rate constants for TCE degradation when hydrogen peroxide and ozone were continuously supplied at rate ratios >0.8 (up to 2.0) mol H_2O_2/mol O_3. They point out that this ratio should not be interpreted as the optimal residual mole ratio of hydrogen peroxide and ozone effecting contaminant degradation, because the residual ozone in the liquid phase varied for systems of different reaction rates. However, Zappi (1995) concluded that molar stoichiometric ratios between 1 and 1.5 were optimal for peroxone systems that employed batch addition of hydrogen peroxide for removing TNT from contaminated waters.

Model Predictions for Various Peroxone Systems

To better understand potential differences in peroxone system performance, the above-proposed steady-state hydroxyl radical concentration model (2.20) was evaluated using a variety of peroxone systems (i.e., ozone and hydrogen peroxide dosing combinations under a variety of buffered pH ranges). The systems modeled were selected to determine an appropriate range of oxidizer concentrations that may be evaluated during laboratory experimentation. Emphasis was placed on oxidizer concentrations without extreme pH effects (i.e., 3<pH<9).

Table 1 lists the first series of model runs that evaluated a constant hydrogen peroxide dose of 10 mg/ℓ and various residual ozone concentrations ranging from 0 to 25 mg/ℓ. The table also presents runs that evaluated the impact of pH on hydroxyl radical concentration. These data clearly indicate that increasing pH should also increase steady-state hydroxyl radical concentration and conversely reaction rate. Increasing pH from 3 to 7 generally increased hydroxyl radical concentrations by 4 orders of magnitude (for $[O_3]$ = 1 mg/ℓ, 10^{-15} to 10^{-11} mg/ℓ). Increasing pH from 7 to 9 results in an approximate 2 order of magnitude increase (for $[O_3]$ = 1 mg/ℓ, 10^{-11} to 10^{-9} mg/ℓ). Although increasing pH beyond 9 is feasible, this practice is generally not considered viable for design of groundwater treatment systems; therefore, pHs greater than 9 were not evaluated during this study. Increasing ozone concentration for pHs 3, 7, and 9 resulted in increased radical concentrations. However, beyond an ozone concentration of 6 mg/ℓ a point a vastly diminishing returns appears because of minimum net increase in steady-state hydroxyl radical concentrations. This indicates that for the 10-mg/ℓ hydrogen peroxide-dosed system, ozone concentrations beyond 6 mg/ℓ would provide little benefit in terms of TNT removal (assuming all TNT removal was due to radical oxidation and not primary oxidation). These predictions do present some shortfalls in terms of the model performance because overdosing with ozone does not yield an adverse effect on steady-state hydroxyl radical concentration. However, the results of the experiments performed during this study indicate that a scavenging effect due to excessive oxidizer presence does occur as witnessed by reduced contaminant removal rate (see Chapters 3 and 4).

Table 1
Model Approximations for SS Hydroxyl Radical Concentrations Maintained Within a 10-mg/ℓ Hydrogen Peroxide-Dosed Peroxone System With Varying Ozone Doses

[Ozone] $[OH^{\cdot}]_{ss}$, mg/ℓ	pH 3 $[OH^{\cdot}]_{ss}$, mol/ℓ	pH 7 $[OH^{\cdot}]_{ss}$, mol/ℓ	pH 9, mol/ℓ
0	0	0	0
0.1	1.05EE-16	1.05EE-11	1.05EE-9
0.25	2.53EE-16	2.53EE-11	2.53EE-9
0.5	4.74EE-16	4.74EE-11	4.74EE-9
1	8.42EE-15	8.42EE-11	8.42EE-9
2	1.38EE-14	1.38EE-10	1.38EE-8
4	2.01EE-14	2.01EE-10	2.01EE-8
6	2.38EE-14	2.38EE-10	2.38EE-8
8	2.62EE-14	2.62EE-10	2.62EE-8
10	2.79EE-14	2.79EE-10	2.79EE-8
25	3.30EE-14	3.30EE-10	2.30EE-8

Table 2 presents model runs that evaluated the same range of ozone concentrations evaluated in the runs listed in Table 1 except that a 100-mg/ℓ hydrogen peroxide dose was for system pHs of 3, 7, and 9. Comparing these results to the

Table 2
Model Approximations for SS Hydroxyl Radical Concentrations Maintained Within a 100-mg/ℓ Hydrogen Peroxide-Dosed Peroxone System With Varying Ozone Doses

[Ozone], mg/ℓ	pH 3 $[OH^{\cdot}]_{ss}$, mol/ℓ	pH 7 $[OH^{\cdot}]_{ss}$, mol/ℓ	pH 9, $[OH^{\cdot}]_{ss}$,mol/ℓ
0	0	0	0
0.1	1.08EE-15	1.08EE-11	1.08EE-9
0.25	2.69EE-15	2.69EE-11	2.69EE-9
0.5	5.35EE-14	5.35EE-10	5.35EE-8
1	1.06EE-14	1.06EE-10	1.06EE-8
2	2.05EE-14	2.05EE-10	2.05EE-8
4	3.89EE-14	3.89EE-10	3.89EE-8
6	5.55EE-14	5.55EE-10	5.55EE-8
8	7.05EE-14	7.05EE-10	7.05EE-8
10	8.42EE-14	8.42EE-10	8.42EE-8
25	1.58EE-13	1.58EE-9	1.58EE-7

10-mg/ℓ hydrogen peroxide dose runs (Table 1) indicates that little benefit is gained by adding higher hydrogen peroxide concentrations until applied residual ozone levels in excess of 2 mg/ℓ are achieved. At this point, the steady-state hydroxyl radical concentration predicted for the 100-mg/ℓ hydrogen peroxide dose (2.052EE-10 mg/ℓ) is approximately 30 percent more than the concentration predicted for the 10-mg/ℓ hydrogen peroxide dose (1.37EE-10 mg/ℓ). The difference in performance increases with increasing ozone dose, while the point of diminishing returns appears to be an ozone dose of 25 mg/ℓ.

Table 3 lists the results of model runs using a 1-mg/ℓ hydrogen peroxide dose for the same ozone doses and pH values evaluated above. These data indicate the point of diminishing returns to be approximately at an ozone dose of 4 mg/ℓ. These data indicate very similar results as observed with the 10-mg/ℓ hydrogen peroxide-dosed systems.

The results of the various model runs indicate that the model appears to be incapable of predicting scavenging reactions by the parent oxidizers (i.e., hydrogen peroxide and ozone). The results of Glaze and Kang (1988) clearly support that these scavenging or termination reactions do occur. The lack of a predictive capability for termination reactions indicates that a key termination step may have been overlooked within the development of the model or that the reaction rates reported by the various research groups are in error. In either case, the model does indicate an upper ceiling of residual ozone concentration beyond which little benefit is gained in increasing ozone concentrations beyond that point (i.e., point of diminishing returns).

Table 3
Model Approximations for SS Hydroxyl Radical Concentrations Maintained Within a 1-mg/ℓ Hydrogen Peroxide-Dosed Peroxone System With Varying Ozone Doses

[Ozone], mg/ℓ	pH 3 $[OH^{\cdot}]_{ss}$, mol/ℓ	pH 7 $[OH^{\cdot}]_{ss}$, mol/ℓ	pH 9, $[OH^{\cdot}]_{ss}$, mol/ℓ
0	0	0	0
0.1	3.64EE-16	3.64EE-12	3.64EE-10
0.2	7.03EE-16	7.03EE-12	7.03EE-10
0.5	1.60EE-15	1.60EE-11	1.60EE-9
1	2.79EE-15	2.79EE-11	2.79EE-9
2	4.44EE-15	4.44EE-11	4.44EE-9
5	6.88EE-15	6.88EE-11	6.88EE-9
10	8.42EE-15	8.42EE-11	8.42EE-9
50	1.03EE-14	1.03EE-10	1.03EE-8

The impact of increasing pH is also observed upon the review of the model runs (Tables 1 through 3). These results indicate that experiments evaluating peroxone's ability to remove TNT should generally be focused between pHs within the neutral to basic range of pHs 7 to 9 with 9 considered a practical upper limit.

The model runs clearly indicate the value of supplying adequate amounts of ozone into the peroxone system. However, ozone generators currently available typically are only capable of producing ozone gas phase percentages within the 1- to 10-percent range with most systems producing 2- to 5-percent ozone. Therefore, steady-state (SS) residual ozone concentrations in excess of 20 mg/ℓ are generally not possible using the generators of today. Recent advances in generator technology indicate that ozone percentages in excess of 30 percent may one day be obtainable, which will vastly improve a given reactors capability.

Summary

According to the proposed mechanisms and model runs, the following predictions with respect to peroxone performance using typical reactor conditions are predicted:

a. The model did not account for termination (scavenging) reactions observed by others during their experiments. This indicates that either an important termination mechanism was overlooked or that the rate constants reported by some for key peroxone-related reactions are inaccurate (it is very likely that both scenarios have occurred).

b. During peroxone or ozonation, pH becomes an important factor, with faster degradation at higher pH. The pH dependence is primarily due to the reaction of $\cdot OH$ with $HO_2^{\cdot-}$ (the k_6 step) being many orders of magnitude faster than with its conjugate acid H_2O_2.

c. With peroxone, higher SS residual ozone concentrations should be maximized to yield fast rates. However, appropriate respective hydrogen doses should be added to prevent possible radical scavenging from occurring.

d. With peroxone, the reaction is likely, as evident in the data table, to show a first-order dependence on ozone over a wide range of hydrogen peroxide doses (i.e., increasing ozone dose will result in a proportional increase in radical concentrations, and in turn, reaction rate.

e. The peroxone experiments performed within this study should focus on a neutral to basic pH range (within practical limits) and hydrogen peroxide doses ranging between 1 and 100 mg/ℓ since SS residual ozone concentrations beyond 8 mg/ℓ were beyond the capability of the ozone generator used in this study and also those typically found within the marketplace.

3 Experimental Methods

Materials

Peroxone pilot system

The peroxone oxidation pilot system (POPS) used in this study was designed and constructed by WES. The system was transported by WES personnel and set up at NBCS for operation. The three test influents were evaluated at this location by WES personnel.

The system has the capability of varying the influent flow rates from 0.5 to 10 gal per min (gpm). Figure 2 presents a schematic of the WES POPS unit. The POPS unit is comprised of the following key components:

a. *A 3-lb per day Orec ozone generator.* This unit is capable of producing a continuous stream of air containing up to 2-percent ozone (wt/wt). Ozone was introduced into the columns via ceramic spargers located on the column bottoms.

b. *Four glass reactor columns.* The columns have 6.0-in. internal diameters and 12.5 ft of reaction column with 1.5 ft of internal free board. All four columns will have capability for both ozone and hydrogen peroxide introduction; however, for this study, hydrogen peroxide was batch added only into Column 1.

c. *A central data logging system control unit.* The heart of this system is a Gateway 486, 200 Mbyte, 50 MHz computer and an on-screen operations analysis program used for system operation and real-time data logging.

d. *Hydrogen peroxide injection system.* This unit was comprised of a hydrogen peroxide metering pump and hydrogen peroxide feed stock reservoir that was used to precisely dose the peroxone system with hydrogen peroxide of varying strengths (depending on the target dosage).

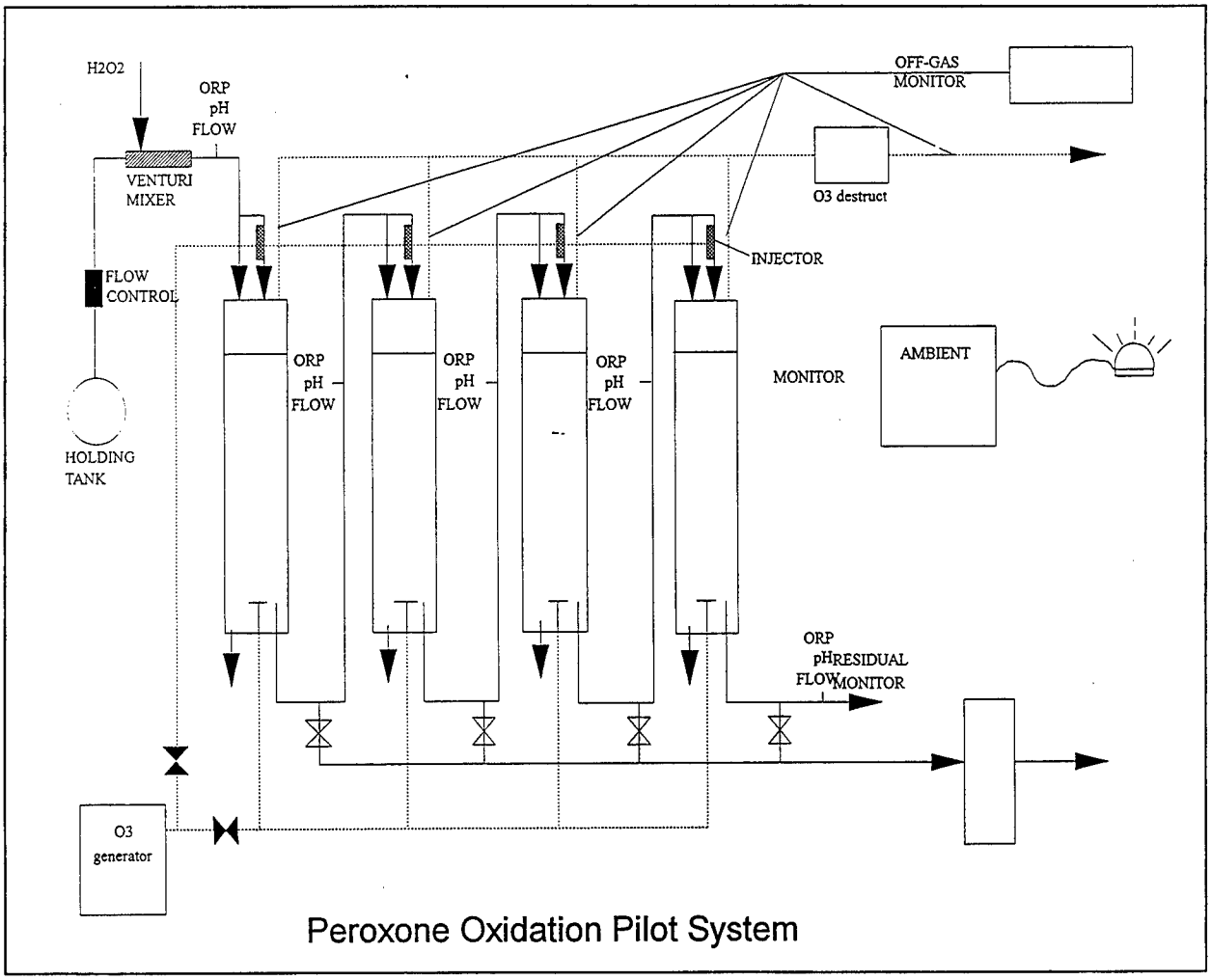

Figure 2. Schematic of POPS unit

e. *Air phase ozone monitors.* Two ozone monitors were used with the system. One unit was used to monitor ozone generator output in percent ozone (wt/wt). The other unit had a multiport capability for analyzing air phase ozone concentrations at various sampling points including column headspace, pre-ozone and postozone destruction unit, and ambient air.

f. *Liquid phase oxidizer monitors.* An in-line ozone monitor with multiport capability was used for analyzing residual ozone levels in the effluents exiting any of the four columns. A residual hydrogen peroxide analyzer was used to ensure that the proper hydrogen peroxide dose was continually being added into the influent at the predetermined targeted concentration.

g. *Ozone destruction units.* Ozone exiting the columns that was not transferred into the column influents was passed through an ozone destruct system to prevent any release of ozone into the ambient air. A granular activated carbon canister was installed after the ozone destruct system to ensure volatile organics did not escape the system. A photoionizer detector

unit was used to monitor both ambient air and the air passing through the ozone destruct system.

h. *Influent introduction system.* A 100-gal stainless steel tank equipped with automated level control sensors was used to maintain a workable volume of influent for the peroxone system. A positive displacement gear pump with controllable flow rate will be used to feed the influent through the columns at preset flow rates. A 10-µm cartridge filter was placed between the gear pump and first column to prevent buildup of oxidized cations and grit within the columns. Pressure gauges throughout the system will be used for detection of head loss due to clogging of feed lines by suspended solids (especially across the cartridge filter).

The system was operated in a countercurrent flow mode with the hydrogen peroxide-dosed influent flowing downward and the ozonated gas flowing upward through the columns. Hydrogen peroxide doses were completely mixed with the test influents using an in-line vortex mixer installed on the influent line to Column 1 (see Figure 1). The fine bubbles (approximately 2 mm in diameter) produced from the ceramic spargers provided intimate contact between the ozonated air and influent. Ozone mass transfer efficiencies in excess of 70 percent were obtained using this design.

Unfortunately, during POPS operation early into the study, the column ozone off-gas and liquid phase ozone monitors malfunctioned due to the extreme heat in the field. Therefore, ozone transfer efficiencies were not calculated except for the first peroxone run evaluated using the NBCS influent. In this case, transfer efficiencies exceeding 70 percent were observed. Aqueous-phase ozone levels were monitored using a portable colormetric test kit.

Several in-line sensors were used to monitor system hydraulics and general water chemistry as treatment proceeded. Process sensors used with the POPS unit included system influent and final effluent pH and oxygen-reduction potential (ORP) monitoring of system influent and all column effluents. Temperature of the influent and full system effluent was also monitored. A flowmeter and totalizer was used to adjust system HRT and ensure that sufficient water has flowed through the system when changing system chemistry (i.e., evaluating various oxidizer concentrations and HRTs).

Study influents

Essentially three independent pilot studies were performed during this effort. The three test influents used in this effort were as follows:

a. *Influent to the NBCS.* The influent to the NBCS was provided to the POPS via tapping of a 3/4-in. plastic hose into the influent feed line to the activated adsorbers within the treatment plant. A solenoid valve was used to regulate flow into the equalization tank on an as-needed basis (i.e., when the level in the equalization was low, water was allowed to flow in).

b. *Well 23311 of the BANS.* This water sample was collected using the submersible pump that was already present within the well that is used for pumping the groundwater into the influent tank of the BANS. When the groundwater was being pumped into the BANS influent tank, no other wells from the BANS dewatering field were being dewatered to ensure only Well 23311 water was in the BANS influent tank. The groundwater was pumped from the BANS influent tank into a 1,500-gal plastic tank mounted on a flat-bed truck using the influent tank pump and then transported to the NBCS for treatment using the POPS. At the POPS site, two additional 1,500-gal tanks served as influent and effluent holding tanks. The treated groundwater from Well 23311 exiting the POPS was collected in the effluent holding tank and transported back to BANS using the tank mounted on the flat-bed truck. The treated groundwater taken back to BANS was pumped into the influent tank of the BANS for passage through the BANS treatment system. This water will be referred to herein as BANS groundwater.

c. *Composite sample of Wells 01061 and 36001.* Groundwater for the third pilot study was collected from Monitoring Wells 01061 and 36001 at equal volumes (50/50). Wells 01061 and 36001 are located in the middle of South Plants Area and the south end of the Basin A Area, respectively. This 50/50 composite was selected because the final concentration of the composite was considered characteristically similar to groundwater quality found within the Basin A and South Plants Areas. The groundwater from each monitoring well was collected by using a portable submersible pump powered from a portable electric generator. The groundwater samples were composited by first filling the tank with Well 01061 groundwater, then pumping Well 36001 groundwater into the tank. The mixing eddies caused by injection of the groundwaters into the tank ensured complete mixing of the two groundwater samples into a well-mixed sample. This water is referred to herein as the South Plants (SP) groundwater.

Chemical Analysis

The analytes and respective methods used for analysis of water samples collected are listed below. Also listed below is the test location and the respective analyte category sampled for during the pilot studies performed at that site. Table 4 lists the detection limit for the various analytes monitored during the peroxone studies. As stated earlier, these limits will be used as the targeted treatment goals for process evaluation.

DIMP

DIMP analyses were performed by the Analytical Laboratory at RMA using Analytical Method No. RMA 33. DIMP samples were collected in precleaned 1-ℓ,

Table 4
Method Detection Limits and Study Target Treatment Goals for the RMA Peroxone Pilot Studies

Analyte	Detection Limit, µg/ℓ
Benzene	0.5
Chloroform	0.5
Chlorobenzene	0.5
1,2-Dichloroethene	0.5
Methylene Chloride	0.5
Trichloroethene	0.5
n-Nitrosodimethylamine	0.012
Diisopropylmethylphosphonate	1.78
Dibromochloropropane (nemagon)	0.05
Aldrin	0.04
Dieldrin	0.04
Endrin	0.04

Note: These treatment goals were set by WES solely for the purpose of comparing various peroxone systems to each other. These limits do not infer any agreement or acceptance of a goal by the RMA or the U.S. Army.

The detection limits listed above were the standard detection limits allowable by each method. Complex water matrices, such as SP groundwater, may have slightly higher limits. As the water becomes cleaner during treatment, these limits typically are reduced. Appendix A lists the raw data that present the actual limits for a given water sample with BDLs.

glass bottles and submitted directly to the RMA laboratory within 2 days of the sample collection. During storage, the samples were stored in a refrigerator set at 4 °C.

VOCs

Volatile organics analyses (VOAs) were performed by both the RMA Analytical Laboratory and the Environmental Chemistry Branch (ECB), WES. Two laboratories were used because of the large number of analyses required within the short period of time the pilot studies were performed. Samples were collected in 40-ml amber VOA vials and delivered to both laboratories within a 48-hr period. Samples were analyzed using Analytical Method USEPA 8240. Samples were stored at 4 °C until ready for shipment to the laboratories.

Pesticides

Pesticides were analyzed by the ECB using Analytical Method USEPA 8080. Dibromochloropropane (DBCP) analysis was performed using this extraction and analytical technique. Samples for pesticide analyses were collected in 1-ℓ

precleaned amber bottles. Samples were delivered to the ECB within 5 days of collection. Until shipment, samples were stored at 4 °C.

NDMA

RMA Analytical Laboratory provided n-nitrosodimethylamine (NDMA) analyses via two contract laboratories: DataChem Laboratories, Salt Lake City, UT, and Oak Ridge National Laboratory, Oak Ridge, TN. Samples were collected in precleaned, 1-ℓ, amber bottles. The sample bottles were stored in the refrigerators at 4 °C until shipped to each respective laboratory. Holding times prior to shipment did not exceed 5 days.

Chemical oxidizers

Ozone and hydrogen peroxide were analyzed using two analytical techniques. The first technique used electrochemistry probes that were installed into the POPS system. The second technique was colorimetric-based (Chemetrics, Inc.).

General water chemistry

Temperature, pH, and ORP were analyzed using electrochemical probe techniques. Calibration of the electrochemical probe systems was performed in the field following the manufacturer's guidelines. The pH probes were calibrated using a two-point calibration technique (pH 4 and 10 as standards).

Organic vapors

A photoionizing organic vapors detector (HNU, Model No. 201) was used to measure the organic content of gases exiting the POPS columns, the headspace of the influent equalization tank, and the gases exiting the activated carbon adsorbers treating the off-gases exiting the POPS columns (analyzed at a minimum of three times daily). This unit was calibrated at RMA following the manufacturer's guidelines and using a benzene surrogate. The detection limit of the photoionization detector 0.1 ppm for organic vapors. Organic vapors were not detected during experimentation in the gas streams exiting the adsorbers, indicating that no organic contaminants were released into the ambient air.

POPS Operation

Peroxone oxidation was operated under a wide variety of conditions. Each condition, referred to herein as a "system," is defined by the amount of hydrogen peroxide and ozone added, the system pH (not adjusted during this study), and HRT. As discussed in Chapter 2, peroxone oxidation is sensitive to the relative amounts of ozone and hydrogen peroxide present in the reactor (often referred to as

the stoichiometric ratio of reactants). Either oxidizer can be present in insufficient or excessive amounts. The ratio of hydrogen peroxide to ozone dosed into the system is referred to herein as the H/O ratio. Various H/O ratios were investigated during this study using the POPS unit. The H/O ratios were varied by adjusting the hydrogen peroxide dose added to the influent and/or the percentage of ozone sparged into each of the POPS columns. Since hydrogen peroxide was batch added and ozone was continuously sparged into the system, it can be said that the system is semibatch with regard to the parent oxidizers. Since the system was operated as a semibatch system, the H/O ratios were constantly changing as the hydrogen peroxide was being degraded in the presence of ozone during passage of the waters through the columns.

Several test systems were evaluated using the POPS. However, once the POPS was set up and the test influent pumped through the system, various hydrogen peroxide and ozone doses were evaluated as a means of evaluating the "oxidizer sink" associated with each water. Based on these experiments, several test systems were selected at the site. As the POPS was adjusted from one test system to another, at least two reactor volumes were allowed to pass through the POPS to ensure that steady-state conditions were reached before samples were collected. This ensured that treatment conditions representative of the targeted system were established prior to sample collection. Testing of effluents exiting each POPS column for both hydrogen peroxide and ozone was conducted after two reactor volumes was performed until three consecutive readings of the same value were recorded indicating complete system stability (steady state). After that point, analytical samples were collected.

The test systems evaluated for each test influent are listed in Tables 5 through 7. The tables list the sampling locations, the number of replicates collected, and targeted analytes for which each sample was analyzed. Sampling locations and the level of sample replication varied for the various runs based on the observed performance of the POPS during field operations. Since a finite number of analytical samples were arranged prior to field operation, emphasis was placed on those peroxone systems that were believed during field operations to provide the most information in terms of optimum system performance.

During shipment of the analytical samples to WES and the RMA contract laboratories, some of the sample bottles were broken during transit. Although, significant measures were undertaken such as packing the ice chests with bubble-wrap, bottles were still lost. Other samples were lost because one of the walk-in coolers at WES that were storing samples awaiting analysis malfunctioned by freezing several bottles and VOC vials until breakage occurred. These samples were considered unsalvageable and were not analyzed.

Table 5
Summary of NBCS Groundwater Peroxone Systems Evaluated

System HRT min	$[H_2O_2]$ Dose mg/ℓ	Ozone Content percent	Columns Sampled	Analytes and Extent of Replication
90	500	2	I	1V, 3P, 2D, 2N
			1	1V, 3P, 3D, 2N
			2	1V, 3P, 3D, 2N
			3	1V, 3P, 3D, 2N
			4	1V, 3P, 3D, 2N
90	250	2	I	1V, 0P, 3D, 1N
			1	1V, 0P, 3D, 1N
			2	1V, 2P, 3D, 1N
			3	1V, 2P, 3D, 1N
			4	1V, 2P, 3D, 1N
90	100	2	I	3V, 3P, 3D, 2N
			1	3V, 3P, 3D, 2N
			2	3V, 3P, 3D, 2N
			3	3V, 3P, 3D, 2N
			4	3V, 3P, 3D, 2N
60	100	2	I	1V, 0P, 2D, 0N
			1	1V, 0P, 2D, 0N
			2	1V, 0P, 2D, 0N
			3	1V, 0P, 2D, 0N
			4	1V, 0P, 2D, 0N
90	10	2	I	1V, 3P, 3D, 1N
			1	1V, 3P, 2D, 1N
			2	1V, 1P, 2D, 1N
			3	1V, 2P, 3D, 1N
			4	1V, 2P, 2D, 1N
90	100	None	I	1V, 0P, 2D, 2N
			4	1V, 0P, 2D, 2N

Note: The numbers in front of the analyte descriptors indicate the extent of sampling replication.
V = Volatile organic compounds; P = Pesticides; D = DIMP; N = NDMA; I = Influent sample.

Table 6
Summary of BANS Groundwater Peroxone Systems Evaluated

System HRT min	$[H_2O_2]$ Dose mg/ℓ	Ozone Content percent	Columns Sampled	Analytes and Extent of Replication
90	500	2	I	2V, 0N, 3D
			1	2V, 0N, 3D
			2	2V, 0N, 3D
			3	2V, 0N, 3D
			4	2V, 0N, 3D
90	250	2	I	3V, 2N, 3D
			1	3V, 0N, 3D
			2	3V, 2N, 3D
			3	3V, 0N, 3D
			4	3V, 2N, 3D
90	100	2	I	3V, 2N, 3D
			1	3V, 2N, 3D
			2	3V, 2N, 3D
			3	3V, 2N, 3D
			4	3V, 2N, 3D
90	100	1	I	3V, 2N, 0D
			1	3V, 0N, 0D
			2	3V, 2N, 0D
			3	3V, 0N, 0D
			4	3V, 2N, 0D
90	50	1	I	2V, 2N, 3D
			1	2V, 0N, 3D
			2	2V, 2N, 3D
			3	2V, 0N, 3D
			4	2V, 1N, 3D

Note: The numbers in front of the analyte descriptors indicate the extent of sampling replication.
V = Volatile organic compounds; P = Pesticides; D = DIMP; N = NDMA; I = Influent sample.

Table 7
Summary of SP Groundwater Peroxone Systems Evaluated

System HRT min	$[H_2O_2]$ Dose mg/ℓ	Ozone Content percent	Columns Sampled	Analytes
90	None	None	I	3V, 3P
			1	2V, 3P
			2	2V, 3P
			3	1V, 3P
			4	0V, 3P
90	250	2	I	3V, 3P
			1	3V, 3P
			2	3V, 3P
			3	3V, 3P
			4	3V, 3P
90	100	2	I	3V, 3P
			1	3V, 3P
			2	3V, 3P
			3	3V, 3P
			4	3V, 3P
90	100	1	I	3V, 3P
			1	3V, 3P
			2	3V, 3P
			3	3V, 3P
			4	3V, 3P
90	50	1	I	3V, 3P
			1	3V, 3P
			2	3V, 3P
			3	3V, 3P
			4	3V, 3P

Note: The numbers in front of the analyte descriptors indicate the extent of sampling replication.
V = Volatile organic compounds; P = Pesticides; I = Influent sample.

4 Results

The results of the experiments performed on the three groundwaters are presented and discussed separately below. As stated earlier, an evaluation based solely on technical merit in terms of contaminant removal will be discussed. Targeted treatment goals for each contaminant in the context of this study were selected as removal to BDLs of the respective analytical method used for each contaminant as indicated in Table 4.

The results of the various peroxone pilot runs are presented in the form of concentration versus test time (C-T) plots in the body of the report. Each data point on the plots represents an average of the replicate sampling events. Appendix A presents the raw data tables that list the results of each individual replicate sampling event. The plots present the method detection limit for the contaminant if the initial contaminant concentrations were close to the method detection limit. In some cases, data points are presented that are less than the method detection limit illustrated in the C-T plots. This is possible because the data points presented represent the average of replicate samples for each system evaluated. Averages below the detection limit occur when one or more of the samples were analyzed as below the detection limit with one or more of the other replicates having detectable amounts of contaminant present. In this case, the samples with less than method detection limit values were assigned a concentration value of one-half of the numerical value of the method detection limit. For example, if the detection limit for endrin was 0.07 µg/ℓ and a sample was reported as less than the detection limit, then that sample was given a numerical value of 0.035 for use in the calculation of the average for that sampling event.

North Boundary Containment System

Table 8 lists the contaminants detected in the test influents (including the NBCS influent) during POPS operation at the NBCS. These data represent the average of all the influent contaminant levels for the various test systems evaluated. Table 8 shows that DIMP, NDMA, chloroform, nemagon, dieldrin, and endrin were the primary contaminants present in the NBCS influent.

Table 8
Major Constituents Detected in Study Influents

Analyte[1]	NBCS	BANS	SP
Benzene	ND	ND	67.2
Chloroform	25.32	1,000	2,029
Chlorobenzene	ND	ND	718.75
1,2-Dichloroethene	25	16.5	ND
Methylene Chloride	ND	ND	94.33
Trichloroethene	ND	ND	118
n-Nitrosodimethylamine	0.309	2.41	NA
Diisopropylmethylphosphonate	49.35	705.43	NA
Nemagon	0.027	NA	66.15
Aldrin	0.057	NA	0.39
Dieldrin	0.35	NA	3.04
Endrin	0.144	NA	0.70

Note: NBCS = North Boundary Containment System; BANS = Basin A Neck System; SP = South Plants; ND = not detected; NA = not analyzed for.
[1] All concentrations listed as µg/ℓ.

The NBCS groundwater provided some interesting observations upon the initial start-up of the POPS unit. Initially, only ozone was supplied to the POPS without hydrogen peroxide addition. The NBCS influent immediately changed to a bright pink color. The pink color persisted throughout the POPS unit (i.e., over 80 min of ozonation). To evaluate if the coloration was due to incomplete oxidation associated with sunlight-induced photodecomposition in the presence of the ozone, a 1,000-ml graduated cylinder was filled in the dark (inside a cardboard box) with the NBCS influent and then sparged with ozone for 15 min in the dark. After 15 min of ozonation in the dark, the pink color was present indicating that the color was likely a by-product of ozonation alone and not photo induced. Later discussions with organic chemists[1] indicated that many phosphate-based organics (such as DIMP) can oxidize into several phosphate by-products that will impart a pink tint. Therefore, it is believed that the pink color was probably a phosphate-based intermediate. This issue was not further investigated because as soon as hydrogen peroxide was introduced into the ozonated columns, the pink color was rapidly removed. In fact, as the hydrogen peroxide front appeared to move through the four columns, the pink color was removed resulting in a very clear effluent. The removal of the pink intermediate further exemplified how powerful an oxidizer the hydroxyl radical is compared with ozonation alone.

[1] Personal Communication, 1994, Dr. Tom Jenkins, U.S. Army Cold Regions Research and Engineering Laboratory, Hanover, NH, and Dr. Mohammad Qasim, U.S. Army Engineer Waterways Experiment Station, Vicksburg, MS.

A run was made with the NBCS water where 100 mg/ℓ of hydrogen peroxide was dosed into the system while air only was sparged through the columns to evaluate solar photolytic and volatilization losses of DIMP, NDMA, and chloroform. The results of each of these efforts will be discussed under the respective contaminant discussion section.

Table 9 presents the flow rates and influent/effluent pH values for each NBCS run performed. Table 9 shows that the actual flow rates were similar to the targeted flow rates of 0.85 gpm, allowing for direct comparison of system HRTs. Note that one run was operated at 2.2 gpm to better evaluate removal at a total system HRT of less than 60 min.

Table 9
Summary of Water Chemistry and Flow Rate During NBCS Runs

Peroxone System	System Flow gpm	Influent/Effluent pH	Influent Tank Headspace HNU Readings	Column 1 Off-Gas HNU Readings	Columns 2-4 Off-Gas HNU Readings
100HP/0OZ	0.90	7.60/7.30	NA	NA	NA
10HP/2OZ	0.80	7.60/8.30	NA	NA	NA
100HP/2OZ	2.20	7.80/8.30	NA	NA	NA
100HP/2OZ	0.84	7.58/8.23	NA	NA	NA
250HP/2OZ	0.90	7.50/8.30	NA	NA	NA
500HP/2OZ	0.80	7.70/8.30	NA	NA	NA

Note: HP = Hydrogen peroxide dose, mg/ℓ; OZ = ozone content in sparge gas, percent; NA = not analyzed for.

The pH values indicate a slight increase in pH across the system for all of the runs (typically 7.5 to 8.2) except for the nonozonated run. This increase was observed for each run with all three groundwaters tested during this study. The rationale for this increase is not known; however, there should not be adverse consequences associated with this slight increase in pH. One possibility is that the free hydrogen ions in solution may have been involved with acid-base reactions associated with bicarbonates and/or free cations, thereby reducing the amount of free hydrogen ions available. This reduction will in turn increase pH since pH is by definition the -log [H+].

Oxidizer fate

Figures 3 and 4 present the fate of hydrogen peroxide and ozone within the peroxone systems operated using a total system HRT of 90 min (approximately 0.8 gpm). The peroxone run that was operated at a 60-min HRT (100-mg/ℓ hydrogen peroxide, 2-percent ozone dosed) was not plotted because only 10 percent was degraded in 30 min with approximately 30 percent being degraded within the full

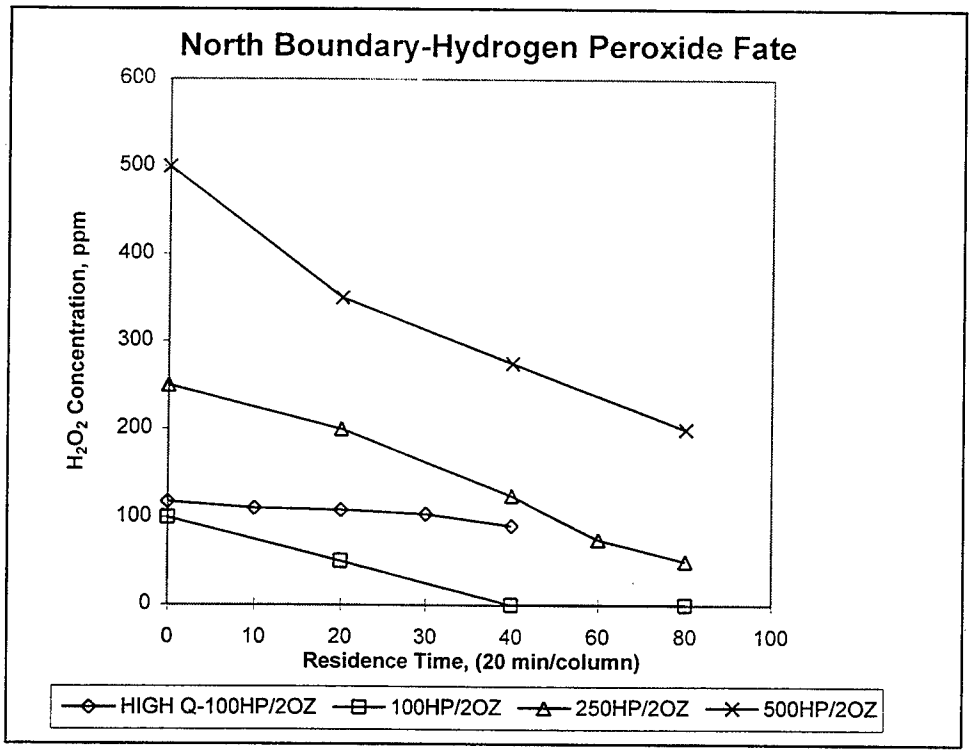

Figure 3. Hydrogen peroxide fate during NBS

60-min HRT evaluated. Conversely, within 60 min of treatment, all of the hydrogen peroxide within the 90-min HRT, 100-ppm hydrogen peroxide, 2-percent ozonated system was degraded to less than 1-ppm levels within 60 min (see Figure 3).

The rationale for this difference is not known. It may be associated with differing chemical matrices since the two systems actually treated water that was collected from the NBCS on different days. The NBCS uses over 50 dewatering wells that are activated on an as-needed basis allowing for differing well input flows into the NBCS sump that can impact general water chemistry. For the sake of comparison for this study, it was assumed that the water chemistry was generally identical. Review of Table 8 indicates that this is a good assumption with regard to contaminants. However, nonregulated compounds, such as bicarbonate and iron, were not monitored; yet these species may have been the cause for hydrogen peroxide to degrade at a different rate within the same system type.

The hydrogen peroxide concentrations exiting Column 1 for all of the systems were unintentionally not recorded. The Column 2 through 4 data indicate that hydrogen peroxide degradation appears to follow zero order kinetics (Figure 3). Zero order kinetics means that the rate of hydrogen peroxide is independent of the concentration of hydrogen peroxide present. This is consistent with observations made by Zappi (1995) during peroxone treatment of TNT-contaminated waters.

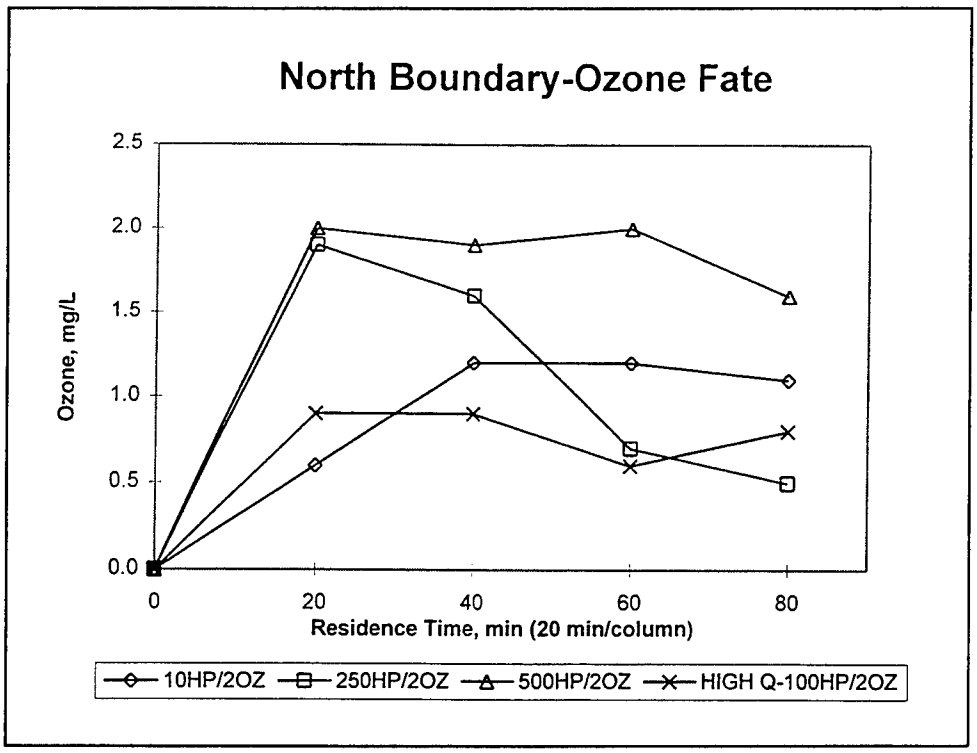

Figure 4. Ozone fate during NBCS runs

Figure 4 presents the ozone concentration data for all of the systems except for the 100-ppm hydrogen peroxide/2-percent ozone systems. The 100-ppm, 90-min HRT ozone concentrations were not recorded because the ozone residual monitor malfunctioned early into this run.

From Figure 4, the ozone levels generally remained at levels approaching 1-2 mg/ℓ. The 250-mg/ℓ hydrogen peroxide/2-percent ozonated system indicated an initial repression in hydrogen peroxide degradation and ozone use (as witnessed by the higher levels of ozone present) followed by a relatively rapid degradation after hydrogen peroxide levels were reduced to sub-200-mg/ℓ levels. The 10-mg/ℓ hydrogen peroxide-dosed system had a very rapid degradation of the hydrogen peroxide to essentially nonexistent levels within the first 20 min of treatment (see Figure 3). After that point, the other columns had ozone levels approximately twice that of those measured in Column 1.

The 500-mg/ℓ hydrogen peroxide-dosed system consistently had the highest ozone levels, indicating a potential slight repression of the ozone-hydrogen peroxide (peroxone) reactions. This will then impact the rate of contaminant removal since the steady-state hydroxyl radical concentrations are decreased within the 500-mg/ℓ dosed system compared with the other system with hydrogen peroxide present at lower levels indicating a higher ozone use rate (i.e., lower steady-state ozone levels).

DIMP removal

Figure 5 presents the DIMP removal data for the NBCS study. These data clearly show that an optimal range of hydrogen peroxide doses exists. The 100- and 250-ppm hydrogen peroxide-dosed systems removed DIMP to BDLs within 40 min of treatment (Column 2). Actually, since DIMP was not detected within the effluents of Column 2 of either the 100- or 250-ppm systems, DIMP was removed within 40 min of treatment and not exactly 40 min as may be assumed based on review of Figure 5. The results of the 60-min HRT, 100-ppm dosed system indicate a system that achieved slower DIMP removal rates than the 90-HRT, 100-ppm system. This observation is consistent with the differences observed in the rate of hydrogen peroxide degradation. It is speculated that possibly the ozone generator may have not been producing preset amounts of ozone. However, since generator output was not continuously monitored during POPS operation, this speculation cannot be confirmed. Future POPS experiments should monitor ozone generator output to eliminate the potential for this to occur. Another potential reason for poorer performance by the 60-HRT system may be the suppression of radical formation reactions due to the presence of a radical scavenger within the influent. Differences in water chemistry between the 60- and 90-min HRT systems are likely since the influent to the NBCS is composed of over 50 dewatering wells that operate in cycled operation based on water levels present within the wells. It could be that dewatering wells containing extraordinarily high levels of radical scavengers (the

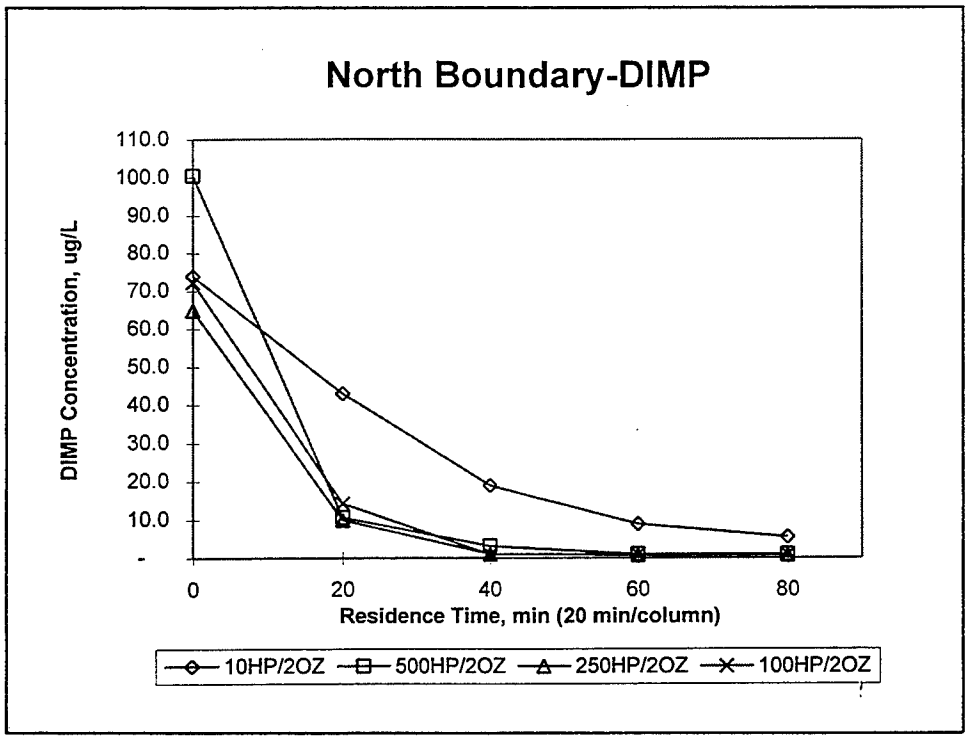

Figure 5. DIMP removal during NBCS runs

actual scavenger species are not known) may have been cycling when the 60-min HRT run was underway.

The 500-mg/ℓ hydrogen peroxide-dosed system indicates that the presence of the additional 250 mg/ℓ of hydrogen peroxide compared with the 250-mg/ℓ dosed run had an adverse impact on DIMP removal as witnessed by the detection of DIMP in the Column 2 effluent. Conversely, the 250-mg/ℓ hydrogen peroxide-dosed system did not have DIMP detected in the Column 2 effluent. This also correlates back to the higher steady-state ozone levels observed within the 500-mg/ℓ dosed system, which are an indicator of slightly repressed peroxone reactions. It is believed that the excessive amounts of hydrogen peroxide present within the 500-mg/ℓ hydrogen peroxide-dosed system (Figure 3) had a scavenging effect on the hydroxyl radicals formed and reductions on the rate of peroxone reactions. However, the scavenging impact of excess hydrogen peroxide is considered minimal because only approximately 10 percent remained after treatment through Column 2. The 10-mg/ℓ dose was obviously too small as observed by the presence of DIMP in the Column 4 effluent (>80 min of treatment).

The difference in performance between the 100- and 250-ppm dose and the 500-ppm dose in terms of DIMP removal is consistent with those observed by Zappi (1995), which observed a slight decrease in performance in TNT removal when increasing the hydrogen peroxide dose in a peroxone system from 200 to 500 mg/ℓ.

The 100-mg/ℓ hydrogen peroxide-dosed, aerated system that was performed as a solar photolysis/volatilization experimental control resulted in only 10-percent removal of DIMP over 80 min of treatment. This low level of removal is likely attributable to some oxidation by the hydrogen peroxide (which was <5-percent degraded within 80 min) and possibly some photolysis. However, based on these results, it can be said that DIMP removal was almost fully attributable to hydroxyl radical-based oxidation.

In summary, the 100- and 250-ppm hydrogen peroxide dose provided the best DIMP removal rates of all of the systems tested. There was no benefit in increasing the hydrogen peroxide dose to 500 mg/ℓ in terms of DIMP removal (and process economics). The 10-mg/ℓ ppm hydrogen peroxide dose was not sufficient to maintain optimal peroxone reactions.

NDMA removal

Figure 6 presents the NDMA removal data for the peroxone systems evaluated. The 60-min HRT, 100-ppm system effluents were not sampled for NDMA (see Table 8).

The 100- and 250-ppm systems performed very similarly by removing the NDMA concentration to approximately BDLs (19 ppt) within 60 min of treatment. The 250-mg/ℓ ppm dose appears slightly superior to the 100-ppm dose since the

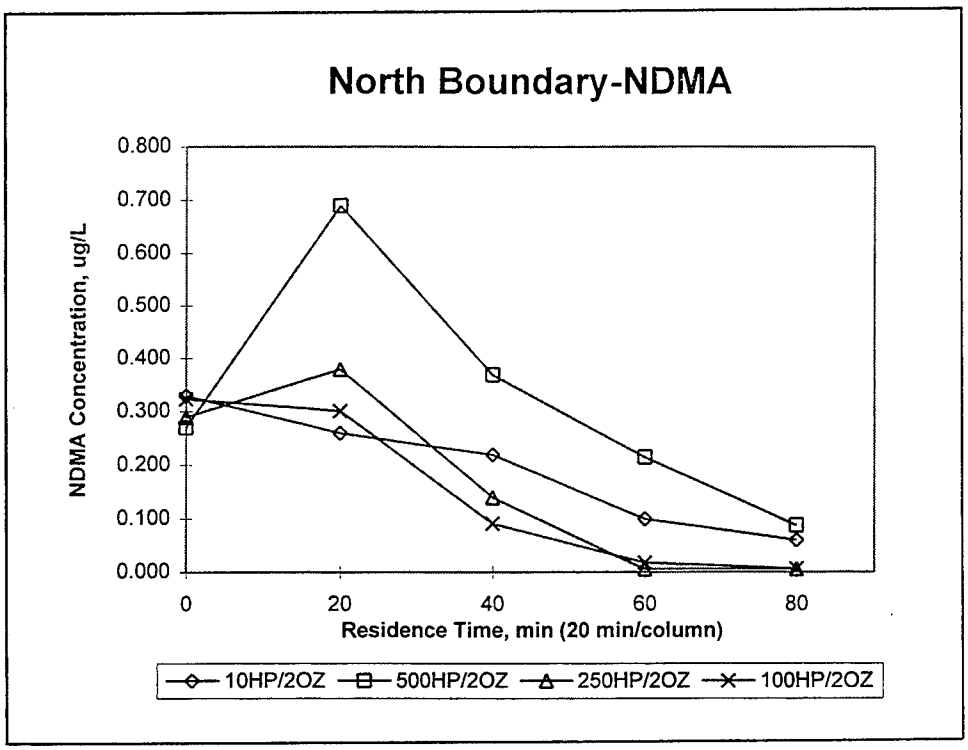

Figure 6. NDMA removal during NBCS runs

100-ppm dose has very low levels of NDMA detected at 60 min. The NDMA data for the 500-ppm dose indicate that the NDMA concentration in the initial sample was lower than the next two data points. These data were generated from two separate sampling events, yet both data sets are within 5 percent of each other. In spite of the increase in NDMA data from the initial sample to the next few data points, the 500-ppm NDMA data indicate that this system achieved removal rates very similar to those obtained with the 100- and 250-ppm doses.

Figure 6 shows that the 10-ppm dose system had dramatically slower removal kinetics than the other systems evaluated. This system was obviously hydrogen peroxide limited, which reduced the rate of hydroxyl radical formation.

The hydrogen peroxide oxidation/photolysis experimental control indicated that 42-percent removal of NDMA occurred within 80 min of treatment. The mechanism for the NDMA removal is likely due to photolysis based on WES past experiences with NDMA.

Endrin removal

Figure 7 presents the results for endrin removal obtained within the peroxone systems evaluated. The figure also indicates the method detection limit for endrin analysis (0.07 µg/ℓ).

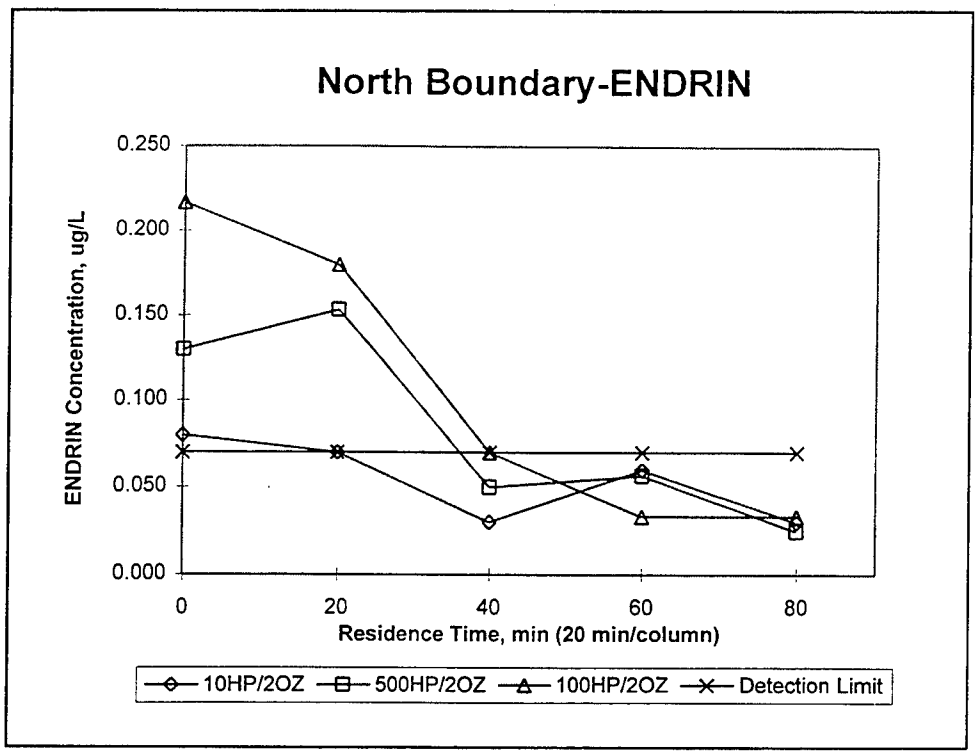

Figure 7. Endrin removal during NBCS runs

The results of the endrin analysis of the column effluent clearly indicate that endrin was easily oxidized by all of the peroxone systems evaluated. There were no distinct differences noted between any of the runs. An HRT between 30 and 40 min of treatment should remove endrin to below detection limit values using any of the peroxone systems tested.

Dieldrin removal

Figure 8 presents the dieldrin data for the NBCS peroxone pilot runs where measurable amounts of dieldrin were detected in the system influent. The 250-mg/ℓ hydrogen peroxide, 2-percent ozone-dosed system did not have measurable amounts of dieldrin present in the influents. Therefore, no dieldrin data for this run were plotted.

From Figure 8, the 100- and 500-mg/ℓ hydrogen peroxide-dosed systems met target treatment goals, while the 10-mg/ℓ dose indicated only slight removal of dieldrin. The 100-mg/ℓ hydrogen peroxide-dosed run had almost three times more dieldrin present in its influent than the 500-mg/ℓ dosed system. Yet, the 100-mg/ℓ dosed system had removed dieldrin down to sub-BDLs within a slightly shorter HRT than the 500-mg/ℓ dosed system. This indicates that the 100-mg/ℓ dosed system provided conditions for a much more rapid removal rate than the 500-mg/ℓ system. The 100-mg/ℓ dose met target levels within 40 min of treatment. The

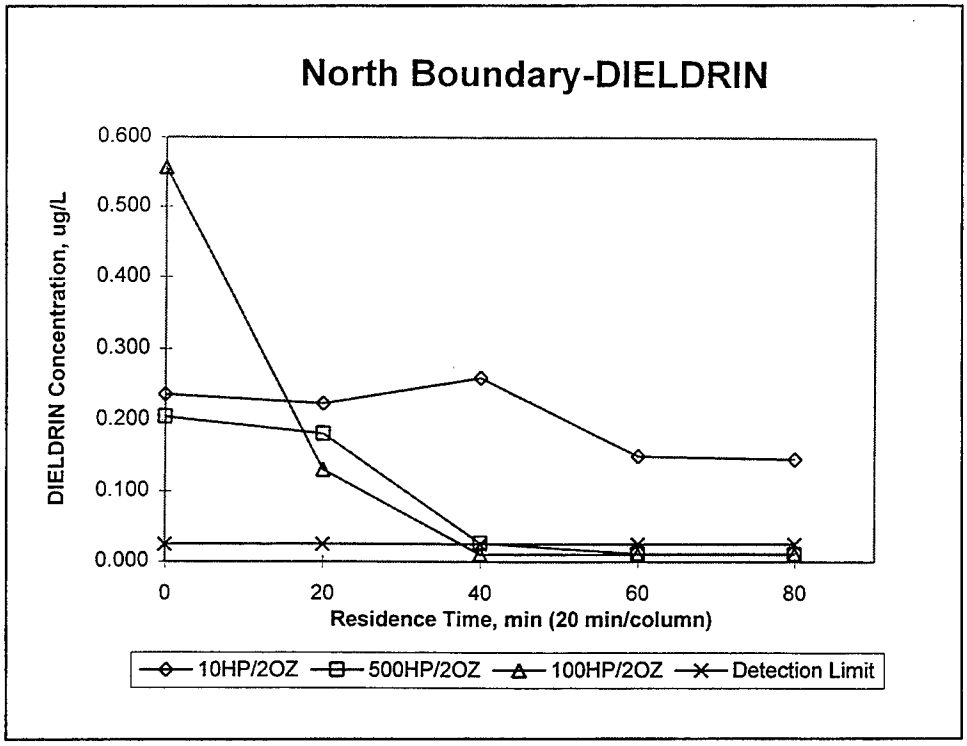

Figure 8. Dieldrin removal during NBCS runs

500-mg/ℓ dose was close to meeting the target levels within 40 min but did require passage through Column 3 (20 more min) before reaching less than detection levels.

Chloroform removal

Figure 9 presents the chloroform data for the peroxone systems tested. Chloroform was not detected in the influent of the 250-mg/ℓ hydrogen peroxide, 2-percent ozone-dosed system.

Chloroform is a volatile compound that is easily removed via air stripping. Sparging of the columns with ozone was expected to result in air stripping being the primary removal mechanism for chloroform. Based on this assumption, it was also expected that all of the peroxone runs would result in almost identical removal rates. However, as shown in Figure 9, this was not the case. The peroxone systems that consistently had positive results, 100-mg/ℓ and 500-mg/ℓ hydrogen peroxide doses, had much better removal rates than the 10-mg/ℓ dose, which consistently performed much more poorly. Also, the hydrogen peroxide-dosed/photolytic experimental control had no chloroform removal within 80 min of treatment, further indicating that for this water, stripping was a minor factor in chloroform removal.

The 100-mg/ℓ and 500-mg/ℓ doses both removed the chloroform to less than detection levels within 20 min of treatment. The 10-mg/ℓ dose required 80 min of

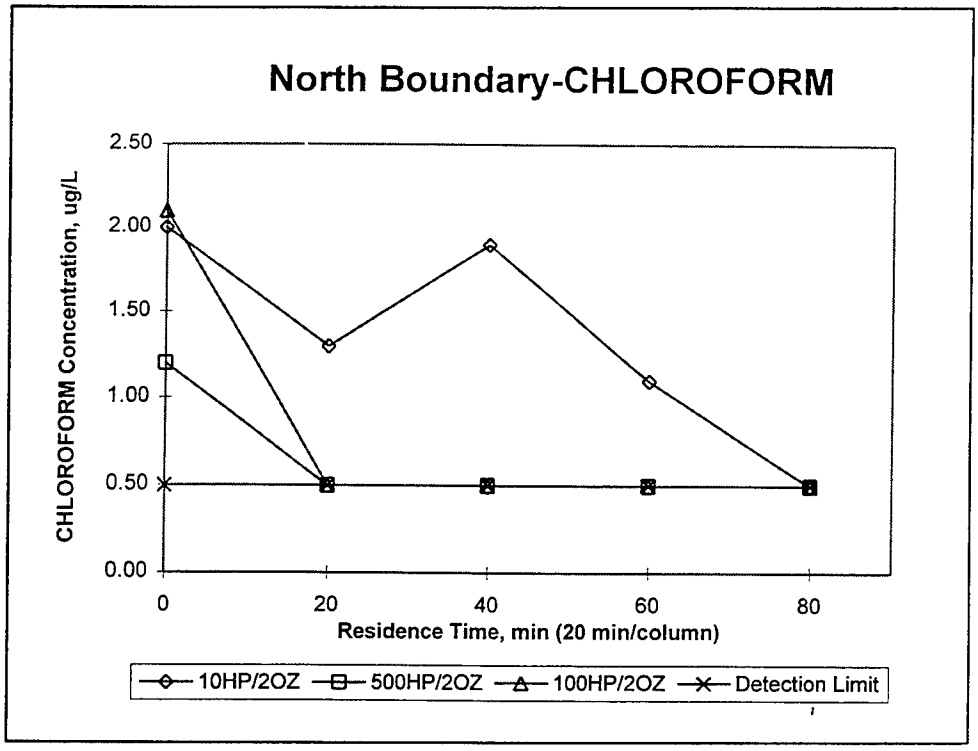

Figure 9. Chloroform removal during NBCS runs

treatment to reach similar treatment. The differences in performance indicate that some oxidation of the chloroform was occurring. The extent of oxidation cannot be quantified without analysis of reactor off-gases, which was not performed during this study.

Summary

Table 10 lists the various HRTs required to meet the target treatment goals for each contaminant for each of the peroxone systems evaluated. From the table, a hydrogen peroxide dose between 100 and 250 mg/ℓ and an ozone composition of 2 percent should meet all treatment goals within 60 min of treatment (i.e., 60-min residence time). The chemical makeup (often referred to as chemical matrix) of the NBCS influent seems amenable to treatment using peroxone oxidation. The potential for using peroxone for treating the NBCS groundwater appears high. Further investigation for the use of peroxone at the NBCS is warranted.

Basin A Neck Groundwater

Table 8 presents the averages of all initial targeted contaminant concentrations detected in the influents for the various peroxone systems evaluated. Table 8 shows

Table 10
Summary of Required HRTs[1] to Meet Target Levels for the NBCS Experiments

Contaminant	High Flow 100H/2OZ	100H/2OZ	250H/2OZ	500H/2OZ	10H/2OZ
DIMP	<80	<40	<40	<60	>80
CHCl3	<40	ND	<20	<20	<80
NDMA	NA	<80	<60	>80	<80
Dieldrin	NA	<40	SL	<20	>80
Endrin	NA	<60	SL	<40	SL

Note: H = Hydrogen peroxide; OZ = ozone; NA = not analyzed for; ND = not detected in influent; SL = sample lost during shipment from RMA.
[1] HRTs in minutes.

that DIMP, NDMA, and VOCs were the primary contaminants found in the BANS groundwater.

Table 11 lists the flow rates and influent/effluent pH values for the BANS runs. As observed with the NBCS water, the BANS water also experienced an increase in pH. The same rationale discussed above for this increase is also proposed for the BANS water.

Table 11
Summary of Water Chemistry and Flow Rate During BANS Runs

Peroxone System	System Flow gpm	Influent/Effluent pH	Influent Tank Head-space HNU Readings	Column 1 Off-Gas HNU Readings	Columns 2-4 Off-Gas HNU Readings
50HP/1OZ	0.86	7.20/7.50	NA	NA	NA
100HP/1OZ	0.86	7.33/7.91	NA	NA	NA
100HP/2OZ	0.90	7.10/7.10	NA	NA	NA
250HP/2OZ	0.90	7.12/7.91	NA	NA	NA
500HP/2OZ	0.90	6.70/7.40	NA	NA	NA

Note: HP = Hydrogen peroxide dose, mg/ℓ; OZ = ozone content in sparge gas, percent; NA = not analyzed for.

From Table 6, these series of experiments evaluated a 2-percent ozonated feed gas content with hydrogen peroxide doses of 100, 250, and 500 mg/ℓ. Two 1-percent ozonated feed gas content runs were also performed that used 50- and 100-mg/ℓ hydrogen peroxide doses. These series of conditions were selected based on field observations that indicated that the hydrogen peroxide demands appeared to be similar to those experienced with NBCS water. The 1-percent ozone-dosed runs

were performed to evaluate the possibility of reducing ozone input that will in turn reduce costs by reducing ozone input and hydrogen peroxide demand.

During treatment of this groundwater sample, the waters in the first two columns turned a milky-white color due to the formation of many microbubbles within the columns. As the water moved through the columns, the color changed to a dark-reddish tint. After the POPS gas flow was turned off, a brownish-yellow precipitant settled out of the water onto the column bottoms. It is believed that the white color was due to the formation of tiny oxygen bubbles due to the breakdown of the hydrogen peroxide by dissolved cations such as reduced iron and manganese. Reactions of this type, such as the iron-hydrogen peroxide reaction (often called Fenton's reaction or reagent), result in the ultimate formation of hydroxyl radicals and water from the hydrogen peroxide and an increase in the oxidation state of the cation (i.e., Fe^{++} to Fe^{+++}). The reddish-brown color is attributed to the oxidized iron and manganese within the columns.

Fate of oxidizers

Figures 10 and 11 present the fate of the hydrogen peroxide and ozone, respectively, during each of the four runs evaluated. Hydrogen peroxide degradation rate, as expected, was dependent on the amount of ozone sparged into the system. The 2-percent ozone-dosed systems all appear to have very similar degradation rates as witnessed by the similarity of C-T slopes (Figure 11). The 1-percent ozone-dosed system also had very similar degradation rates, albeit much slower.

The 50- and 100-mg/ℓ hydrogen peroxide doses added to the 1-percent ozone system lost very little of the hydrogen peroxide through the first 40 min of treatment, while the other systems that used a 2-percent ozone sparge gas lost at least 50 percent of the hydrogen peroxide within a 40-min time span. Only the 500-mg/ℓ dosed run had over 100 mg/ℓ of hydrogen peroxide present in the Column 3 effluent (60 min), indicating potential scavenging of hydroxyl radicals by the excess hydrogen peroxide (see Chapter 1 of this report).

Figure 11 presents the ozone residual concentrations measured in the effluents exiting each column. All of the runs evaluated with the BANS water had ozone levels within the 0- to 2-mg/ℓ range up until 40 min of treatment (passage through Column 2). After 40 min of treatment, the ozone levels began to approach 8 mg/ℓ within the 100-mg/ℓ hydrogen peroxide, 2-percent ozone-dosed system. A residual level of 8 mg/ℓ is the equilibrium liquid phase concentration for the amount of ozone present in the sparge gases. The reason for the increase in residual ozone levels to equilibrium levels was simply that all of the hydrogen peroxide was degraded at 40 min (see Figure 10).

Only the 100-mg/ℓ hydrogen peroxide, 1-percent ozone-dosed and the 500-mg/ℓ hydrogen peroxide, 2-percent ozone-dosed systems had ozone residual levels below 1 mg/ℓ after passage through Column 4 (80 min), indicating significant use of the ozone throughout all four columns for these two systems. In the case of the

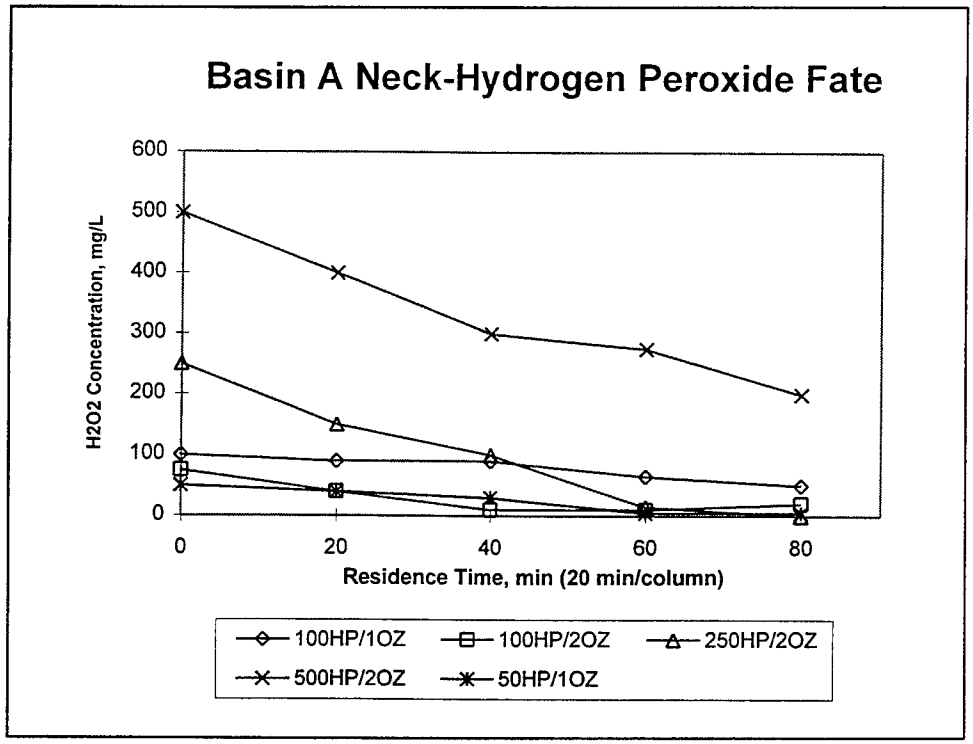

Figure 10. Hydrogen peroxide fate during BANS runs

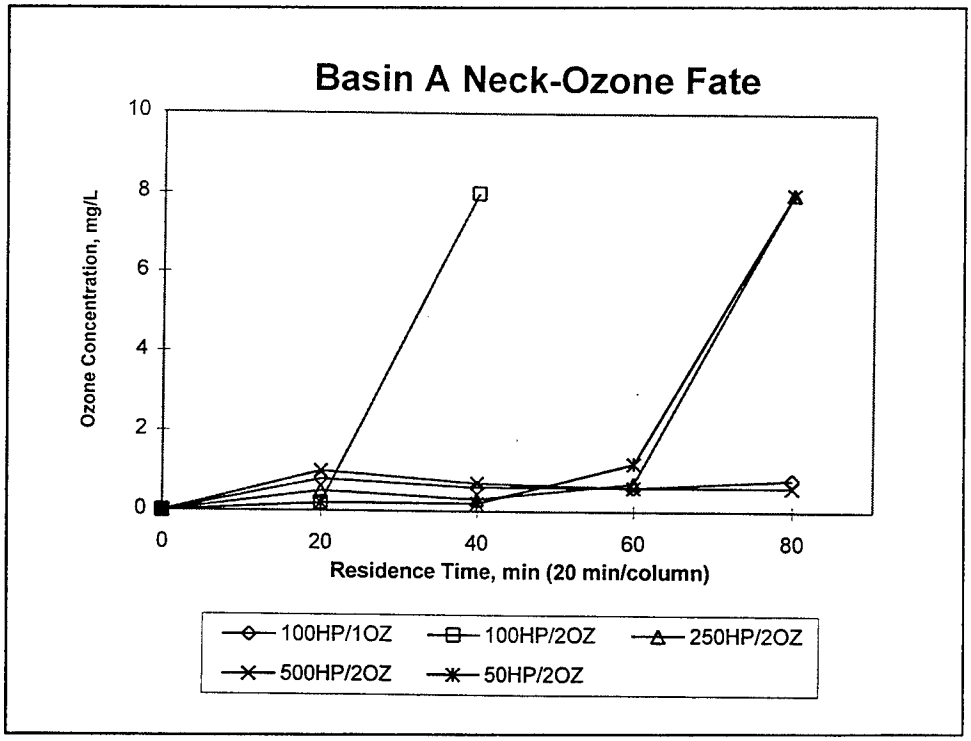

Figure 11. Ozone fate during BANS runs

100-mg/ℓ hydrogen peroxide, 1-percent ozone-dosed system, the reduced amount of ozone (1 percent versus 2 percent) added to the system did not impart a high enough hydrogen peroxide demand to eliminate peroxone reactions. The 500-mg/ℓ dosed system maintained low ozone levels due to the excessive amount of hydrogen peroxide added initially into the system.

DIMP removal

Figure 12 presents the DIMP removal data for the BANS pilot study. As a matter of note, the 100-mg/ℓ hydrogen peroxide, 1-percent ozone-dosed system was not sampled for DIMP removal (see Table 6).

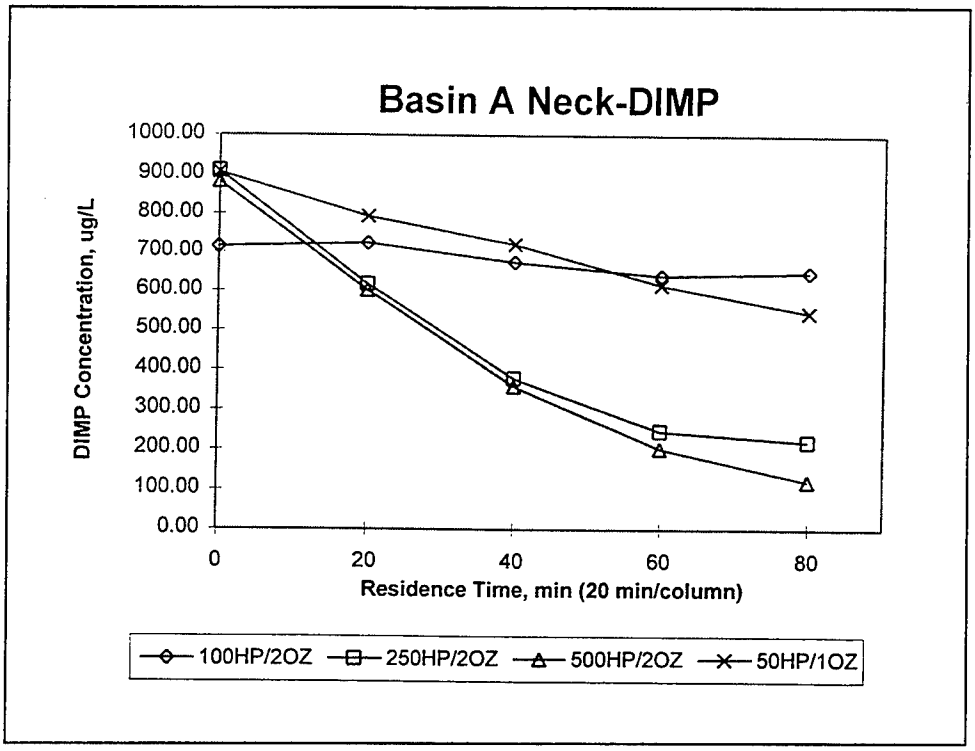

Figure 12. DIMP removal during BANS runs

The two runs that used the highest hydrogen peroxide doses, 250 and 500 mg/ℓ, had higher removal rates than the 50 and 100 mg/ℓ. The 250- and 500-mg/ℓ doses resulted in removals of 75 and 86 percent, respectively. The 250-mg/ℓ dosed run appeared to perform almost identical to the 500-mg/ℓ run until 60 min of treatment (Column 3). From that point on, the 250-mg/ℓ dose clearly began to lose activity toward DIMP. In fact, very little, if any, improvement was made between 60 and 80 min of treatment (Columns 3 and 4) for the 250-mg/ℓ dosed system, indicating that radical formation reaction had indeed ceased by that point. Review of the hydrogen peroxide fate data (Figure 10) indicates that essentially all of the hydrogen peroxide was degraded, which likely caused radical production reactions to cease.

Loss of hydroxyl radical production would in turn eliminate DIMP removal, which is believed to be the case that was observed in Figure 12.

The 50-mg/ℓ, 1-percent ozone- and 100-mg/ℓ, 2-percent ozone-dosed runs performed poorly compared with the 250- and 500-mg/ℓ hydrogen peroxide-dosed runs. The 100-mg/ℓ run performed much more poorly than the 50-mg/ℓ run. The 50-mg/ℓ dose removed approximately 33 percent of the DIMP after 80 min of treatment (i.e., complete passage through the POPS unit), while the 100-mg/ℓ run did not indicate any DIMP removal. The reason for the 50-mg/ℓ dose performing better than the 100-mg/ℓ is not known. Based on the premise that the groundwater had a high hydrogen peroxide demand and the higher doses allowed for more hydrogen peroxide to be available for peroxone reactions, the 50-mg/ℓ dosed run should have performed worse than the 100-mg/ℓ system. One potential reason that the 50-mg/ℓ dosed run performed better than the 100-mg/ℓ run may be that the 100-mg/ℓ dosed run was performed first of all the runs using "fresh" groundwater that had just been collected. The fresh groundwater was not allowed time for the oxidation demand in the groundwater (likely imparted due to the oxidation of the reduced iron) to be met by the oxygen in the air within the tank headspace. The 250-mg/ℓ run was performed next followed by the 500-mg/ℓ and finally the 50-mg/ℓ dosed run. It is possible that aeration via atmospheric oxygen relieved some of the oxidation demand exerted on the hydrogen peroxide.

NDMA removal

Figure 13 presents the NDMA removal data for the BANS groundwater runs. From this figure, it is obvious that peroxone was ineffective in removing the NDMA from the groundwater. The relative complexity of this groundwater when compared with a water such as the NBCS influent likely does not provide a highly aggressive system for removal of difficult to oxidize organic contaminants like NDMA. The 100-mg/ℓ hydrogen peroxide-dosed run, NDMA data showed an increase in NDMA concentration; however, it is believed that this is simply an anomaly in the analytical data.

1,2-DCLE removal

Figure 14 presents the 1,2-dichloroethylene removal data for the BANS runs. There was not a clear optimal peroxone system in terms of 1,2-DCLE removal, indicating that some of the observed removal was likely due to stripping and not oxidation. One run, the 100-mg/ℓ hydrogen peroxide-dosed system, did dramatically differ from the others. From the DIMP data (Figure 12) and the 1,2-DCLE data (Figure 14), the 100-mg/ℓ dosed run was the poorest performer of all those tested. Although, this observation is not surprising due to the lack of hydrogen peroxide present at 40 min (Figure 10). Interestingly enough, the 100-mg/ℓ dosed run initially indicated the most rapid removal (over 50 percent within 20 min), but from that point on, little or no 1,2-DCLE removal was observed. If stripping had been a primary factor, this run would have performed similarly to the others since the same gas flow rate was introduced into the 100-mg/ℓ dosed system as was

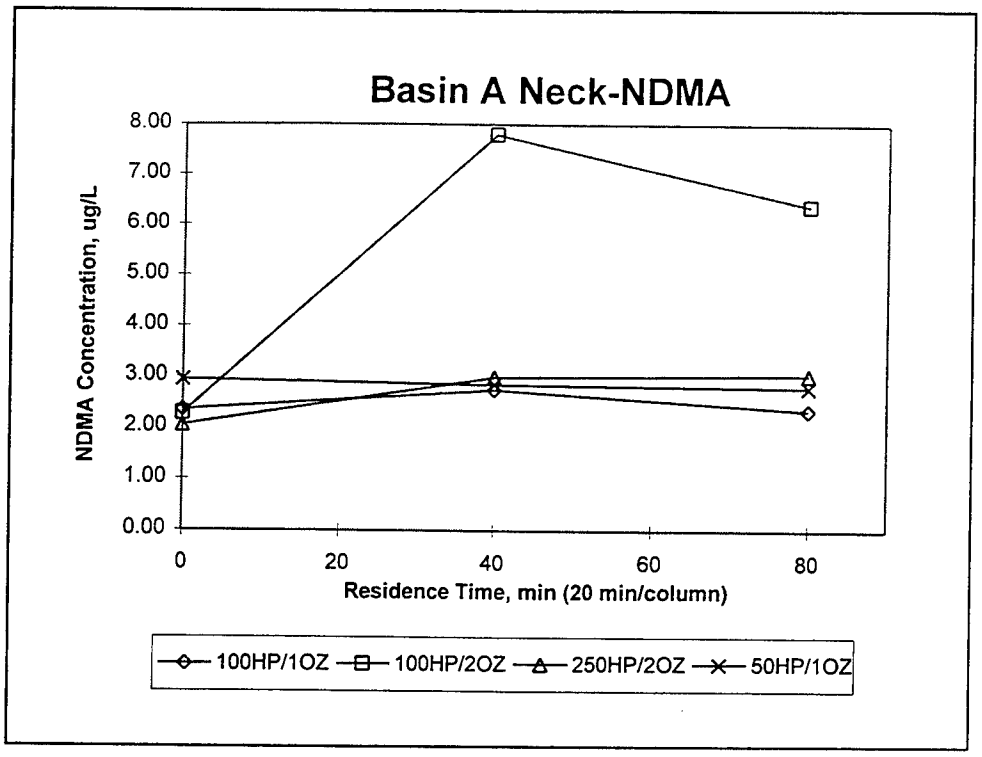

Figure 13. NDMA removal during BANS runs

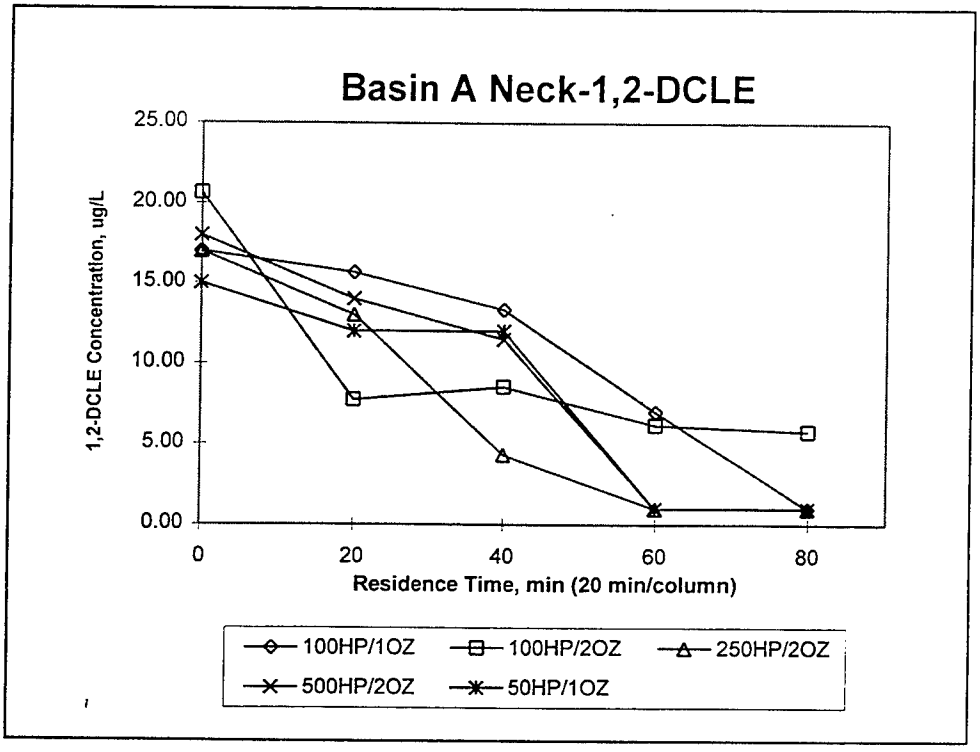

Figure 14. 1,2-DCLE removal during BANS runs

introduced into the other systems. The 2-µg/ℓ target level was met within 60 min by all of the peroxone systems evaluated except the 100-mg/ℓ hydrogen peroxide, 1-percent ozone-dosed system that required the full 80-min HRT to meet this level.

Methylene chloride removal

Figure 15 presents the methylene chloride removal data for the BANS groundwater. The general trend shown with the methylene chloride data follows the same trend observed with the 1,2-DCLE data. The 100-mg/ℓ hydrogen peroxide-dosed system initially had the most rapid removal rate of all the systems evaluated, but after 20 min (Column 1) further methylene chloride removal ceased. Still, the 100-mg/ℓ dose did remove almost 100 percent of the methylene chloride within 20 min. The 250-mg/ℓ hydrogen peroxide-dosed run obtained relatively poor methylene chloride removal by only removing 20 percent for the 80 min of treatment. The 500-mg/ℓ hydrogen peroxide-dosed run resulted in complete removal of methylene chloride, yet this system required the full 80 min of treatment. The 50-mg/ℓ dosed system, which removed over 75 percent within 80 min, outperformed the 250-mg/ℓ dosed system, but achieved less methylene chloride removal than did the 100- and 500-mg/ℓ doses. The vast differences in performance observed with the various peroxone systems tested indicate that stripping did not dominate as the primary removal mechanism for methylene chloride. If stripping was responsible for removal, all of the systems would have performed identically, since the same gas sparge rate was used in all of the runs evaluated.

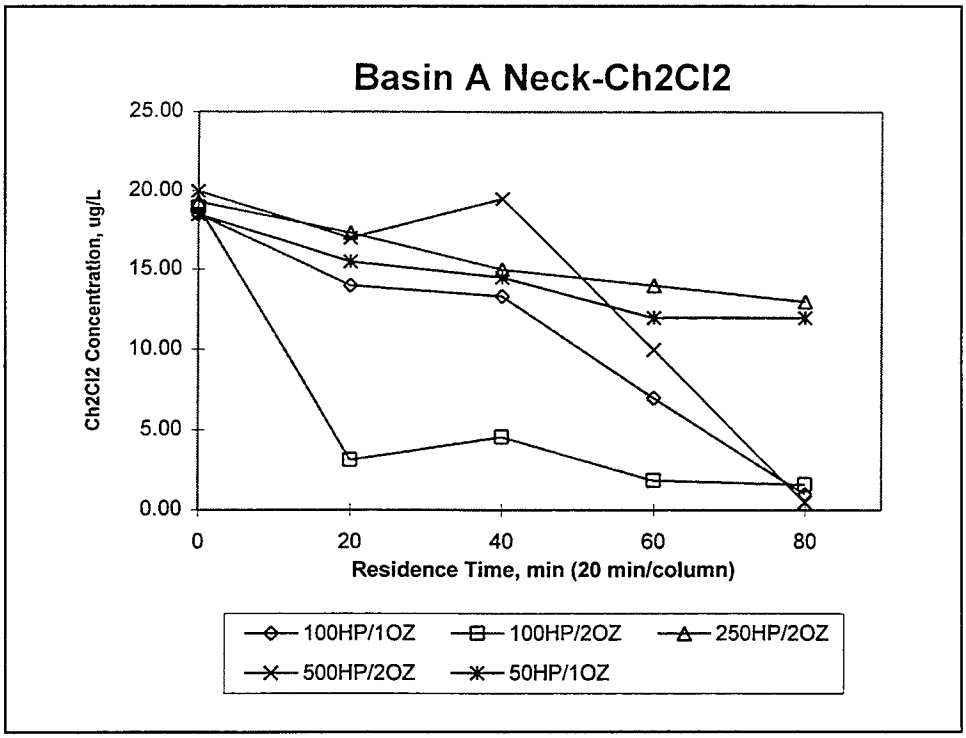

Figure 15. CH2Cl2 removal during BANS runs

Chloroform removal

The chloroform removal data was not plotted because none of the peroxone runs evaluated were able to remove greater than 50 percent of the chloroform; yet since the chloroform started at levels approaching 1,000 µg/ℓ, there appears to be no potential for peroxone to treat the chloroform present in this water at these levels. The 50-mg/ℓ hydrogen peroxide, 1-percent ozone and 250-mg/ℓ hydrogen peroxide, 2-percent ozone-dosed systems were the only two systems evaluated that achieved measurable amounts of chloroform removal by removing approximately 50 and 75 percent, respectively.

Summary

This water sample was much more challenging to peroxone than the NBCS influent. The BANS groundwater had much higher levels of organics plus the presence of reduced iron and manganese likely competed with peroxone reactions for the hydrogen peroxide available. Table 12 lists the HRTs required by each peroxone system to meet the target treatment goals (the table also indicates if they were not reachable within the 80-min HRTs (i.e., >80 min in the table)). There is no potential for application of peroxone at the BANS as a sole treatment source. Peroxone may be considered as a polishing step since the NBCS studies indicated that peroxone can treat the same contaminants found in the BANS groundwater under differing conditions.

Table 12
Summary of Required HRTs[1] to Meet Target Levels for the BANS Experiments

Contaminant	100H/1OZ	100H/2OZ	250H/2OZ	500H/2OZ	50H/1OZ
DIMP	NA	>80	>80	NA	>80
$CHCl_3$	>80	>80	>80	>80	>80
NDMA	>80	>80	>80	NA	>80
1,2-DCLE	ND	>80	<60	<60	<60

Note: H = Hydrogen peroxide; OZ = ozone; NA = not analyzed for; ND = not detected in influent.
[1] HRTs in minutes.

Another interesting point to make concerning the inability of peroxone to meet the target treatment goals for the BANS groundwater is that the contaminants, such as DIMP and chloroform, that eliminate peroxone from consideration as being a potential treatment option for the BANS water are the same contaminants that were easily treated in the NBCS water. This comparison clearly illustrates the impact that concentration levels (i.e., approximately 20 to 40 times higher (Table 8)) and more complex water chemistry (i.e., reduced iron) can have on AOPs.

South Plants Groundwater

Table 8 presents analytical data for the SP groundwater composite. VOCs and pesticides are the predominant contaminant groups that were detected in this sample. The level of both VOCs and pesticides are approximately an order of magnitude higher than those detected in the NBCS influent, which had similar contaminant types.

To select the range of conditions to be evaluated using the SP groundwater, a 100-mg/ℓ hydrogen peroxide, 2-percent ozone-dosed run was first performed. Based on hydrogen peroxide use and ozone use, this system indicated that the SP groundwater had a low oxidizer use rate. Therefore, two runs were performed with 2-percent ozonated air, 100- and 250-mg/ℓ hydrogen peroxide doses, and two additional runs were performed with 1-percent ozonated air, 50- and 100-mg/ℓ hydrogen peroxide.

Table 13 lists the flow rate and influent/effluent pH values for the SP groundwater runs. These data generally follow the same trends observed with the other two waters previously discussed (i.e., good flow replication and an approximate 0.5-pH increase).

Table 13
Summary of Water Chemistry and Flow Rate During SP Runs

Peroxone System	System Flow gpm	Influent/ Effluent, pH	Influent Tank Headspace HNU Readings, ppm	Column 1 Off-Gas HNU Readings, ppm	Columns 2-4 Off-Gas HNU Readings, ppm
0HP/0OZ	0.80	7.60/8.30	<1	49	14
50HP/1OZ	0.85	7.67/8.01	NA	NA	NA
100HP/1OZ	0.85	7.59/8.17	2	40	2.5
100HP/2OZ	0.82	7.60/8.04	30	32	<1
500HP/2OZ	0.86	7.62/7.90	15	35	<1

Note: HP = Hydrogen peroxide dose, mg/ℓ; OZ = ozone content in sparge gas, percent; NA = not analyzed for.

Unlike the other experiments, the HNU PID device was used to assess the extent of volatilization occurring within the POPS system while treating the SP groundwater. These data are also shown in Table 13. If volatilization due to the sparged ozonated air into the reactors was the major mechanism of VOC removal, then by comparing the VOC concentrations within the influent holding tank headspace (which is relatively quiescent) to the headspace gases exiting each column, one could roughly assess how much volatilization of the VOCs was occurring during gas sparging. If the tank headspace VOC levels are greater or equal to those in the column exit gases, then it could be argued that volatilization accounted for minimal VOC removal. On the other hand, if tank headspace levels are much lower than the column exit gases, then volatilization would be the likely removal mechanism.

Review of Table 13 indicates that the 1-percent ozone-dosed systems had much higher levels of VOCs in the column exit gases, thereby providing some evidence that volatilization was a likely removal mechanism. However, the 2-percent ozone-dosed systems generally indicate that oxidation could be considered a primary removal mechanism for the VOCs.

Oxidizer fate

Figures 16 and 17 present the fate data for hydrogen peroxide and ozone, respectively. The hydrogen peroxide data indicate a strong correlation of hydrogen peroxide degradation rate to percent ozone in the sparge gas. The two 2-percent ozone-dosed systems appear to have very similar rates as do the two 1-percent ozone-dosed systems. This trend was also observed with the other waters tested during this effort.

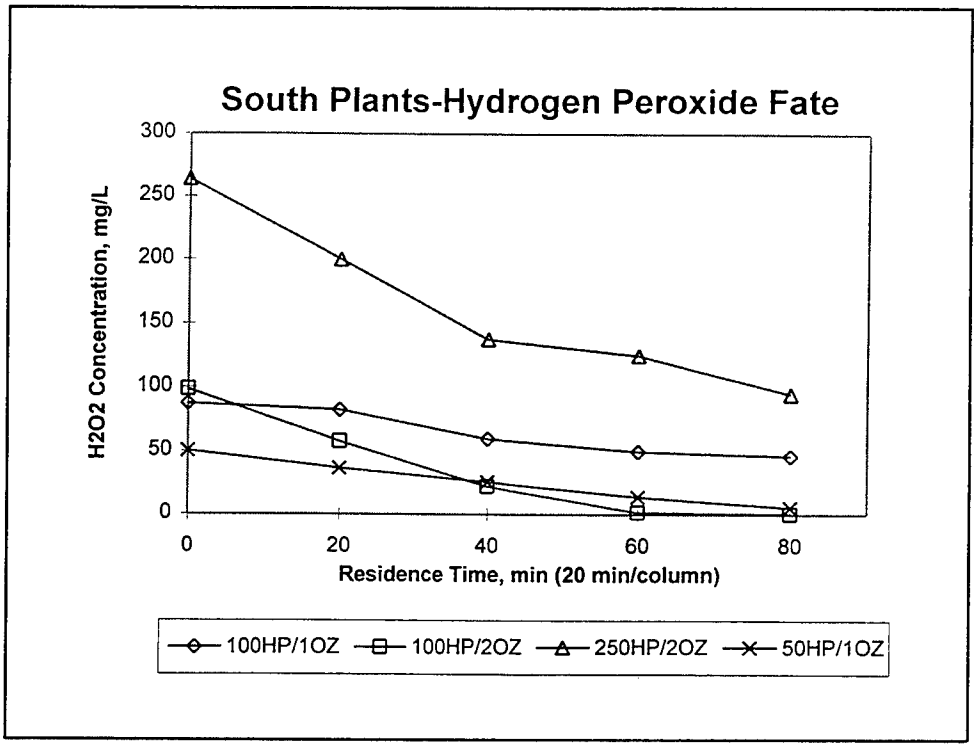

Figure 16. Hydrogen peroxide fate during SP runs

Only the 100-mg/ℓ hydrogen peroxide, 2-percent ozone-dosed system ran out of hydrogen peroxide before the water exited the POPS (80 min HRT). By 60 min of treatment, the 100-mg/ℓ hydrogen peroxide, 2-percent ozone run did not have any detectable hydrogen peroxide present in the Column 3 effluent.

Figure 17 indicates that all of the runs evaluated except the 100-mg/ℓ, 2-percent ozone system had residual levels less than 0.5 mg/ℓ throughout the 80 HRT,

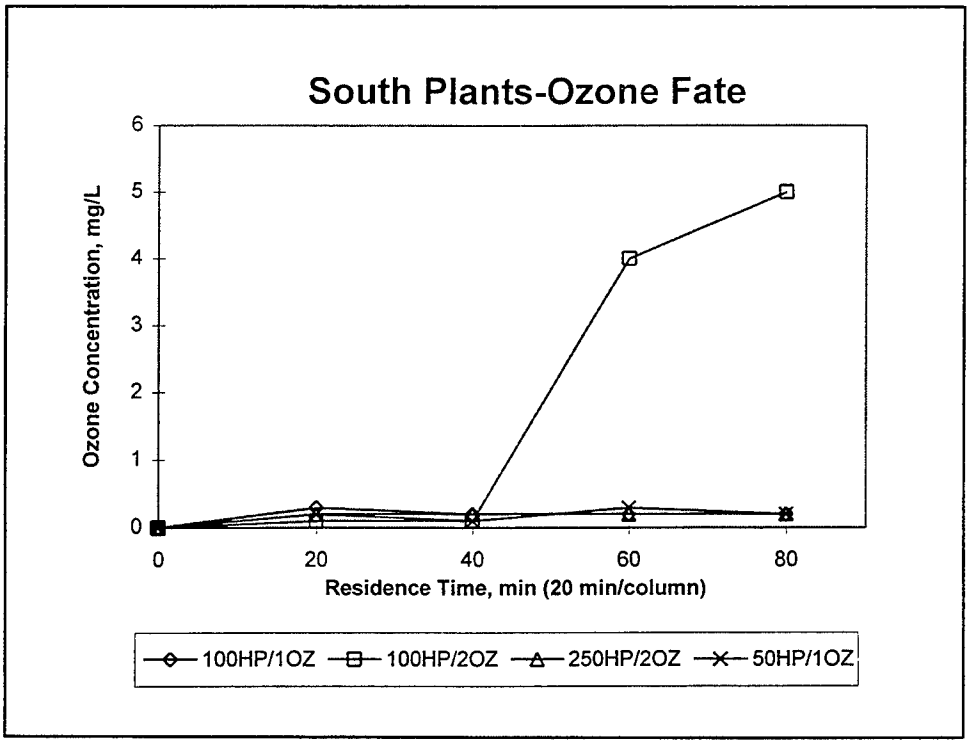

Figure 17. Ozone fate during SP runs

indicating a high use of ozone. The 100-mg/ℓ hydrogen peroxide, 2-percent ozone system had the lowest ozone levels until the 60-min mark (Column 3), when the residual ozone levels jumped to 4 mg/ℓ. The Column 3 effluent (60-min HRT) was also the first point in the system where hydrogen peroxide had fully degraded. At 80 min, the residual ozone level increased to 5 mg/ℓ, indicating that the hydrogen peroxide levels had dropped to amounts too low to sustain peroxone reactions.

Aldrin removal

Figure 18 presents the aldrin removal data for the SP groundwater. The 50-mg/ℓ, 1-percent ozone required the least amount of HRT, 20 min (Column 1), to remove aldrin to BDLs. The 250-mg/ℓ hydrogen peroxide, 2-percent ozone run was the only other system to remove aldrin to BDLs; however, over 60 min were required. The two 100-mg/ℓ hydrogen peroxide-dosed systems both achieved approximately 80-percent removal, but neither system reached detection limit levels within the 80-min HRT.

It is somewhat perplexing why the 50-mg/ℓ hydrogen peroxide, 1-percent ozone-dosed and 250-mg/ℓ hydrogen peroxide, 2-percent ozone-dosed runs performed so similarly to each other. They were not similar in terms of hydrogen peroxide or ozone dosing. No sensible explanation could be proposed; therefore, these data can only be presented and further speculation not made as to the reason for this variance.

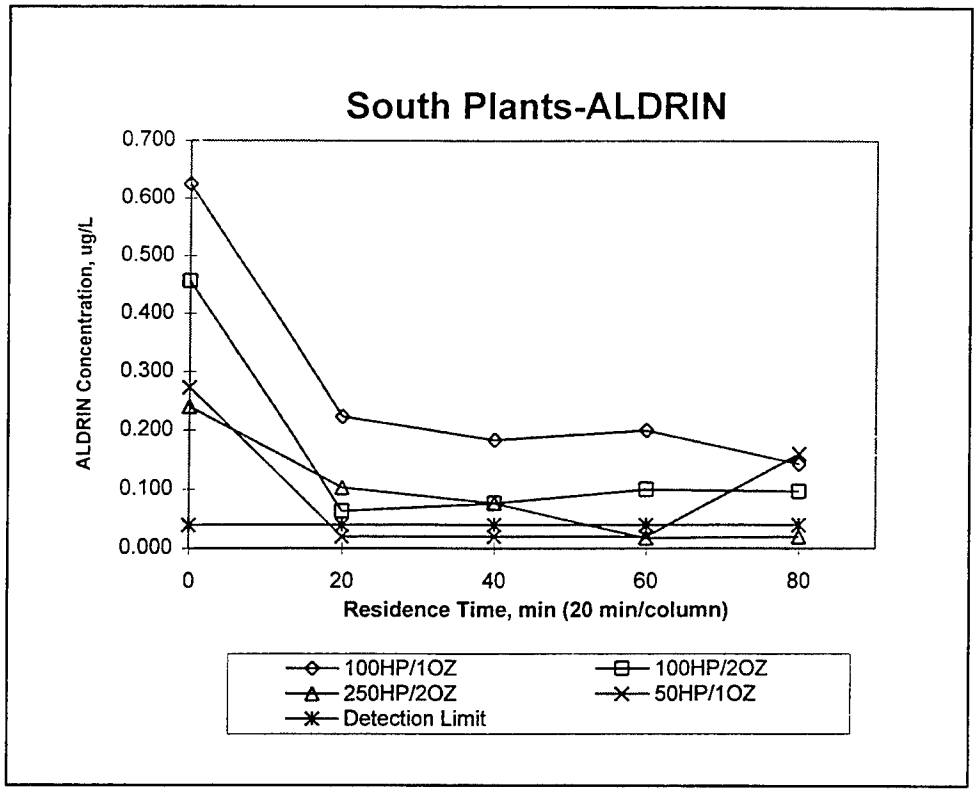

Figure 18. Aldrin removal during SP runs

Dieldrin removal

Figure 19 presents the dieldrin removal data for the SP groundwater. The 2-percent ozone-dosed systems performed much better than the 1-percent ozone-dosed systems. The 2-percent ozone-dosed runs removed approximately 65 percent of the dieldrin within 40 min and approximately 90 percent by 80 min of treatment. The 50-mg/ℓ hydrogen peroxide, 1-percent ozone-dosed system had the slowest removal rate of all the systems tested by only removing approximately 25 percent within 80 min. The 100-mg/ℓ hydrogen peroxide, 1-percent ozone-dosed system removed over 50 percent within 80 min of treatment.

Endrin removal

Figure 20 presents the endrin removal data for the SP groundwater. The 50-mg/ℓ hydrogen peroxide, 1-percent ozone-dosed system did not have detectable quantities of endrin present in the influent; therefore, the data for this system are not plotted in Figure 20.

From Figure 20, the 2-percent ozone-dosed system, once again, had a more rapid removal rate than the 100-mg/ℓ hydrogen peroxide, 1-percent ozone-dosed system.

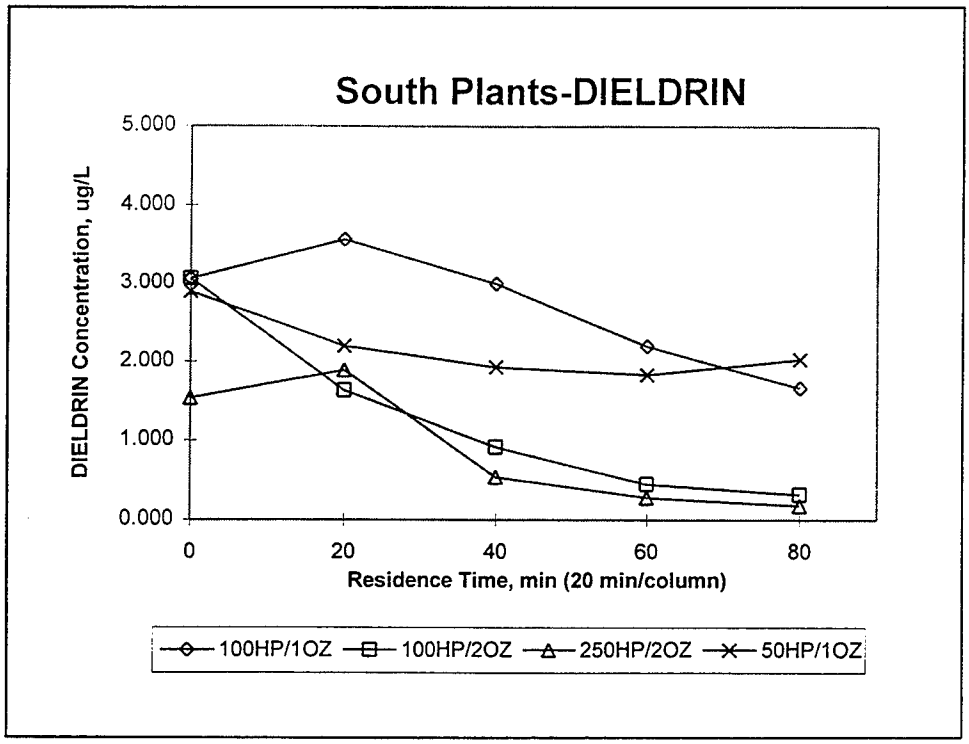

Figure 19. Dieldrin removal during SP runs

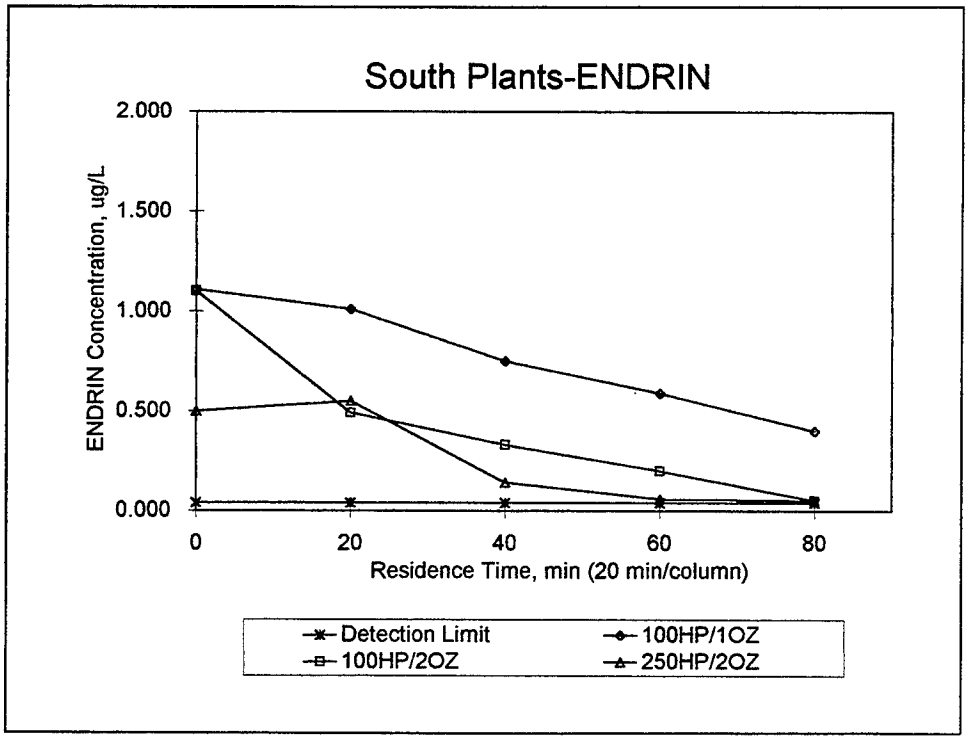

Figure 20. Endrin removal during SP runs

The 250-mg/ℓ hydrogen peroxide, 2-percent ozone-dosed system removed endrin to subdetection limit levels within 60 min of treatment, while the 100-mg/ℓ hydrogen peroxide-dosed system required 20 min longer to reach the same level (80 min). The 100-mg/ℓ hydrogen peroxide, 1-percent ozone-dosed system only removed 50 percent of the endrin within the 80-min HRT evaluated. This system appears to be clearly ozone limited.

Chloroform removal

Figure 21 presents the chloroform removal data for the SP groundwater. All of the systems evaluated performed very similarly in terms of chloroform removal. This indicates that volatilization was the likely predominant removal mechanism for this water. All of the systems removed approximately 60 percent of the chloroform within 80 min of treatment. It appears that much longer HRTs will be required to remove chloroform to detection limit values (0.05 µg/ℓ).

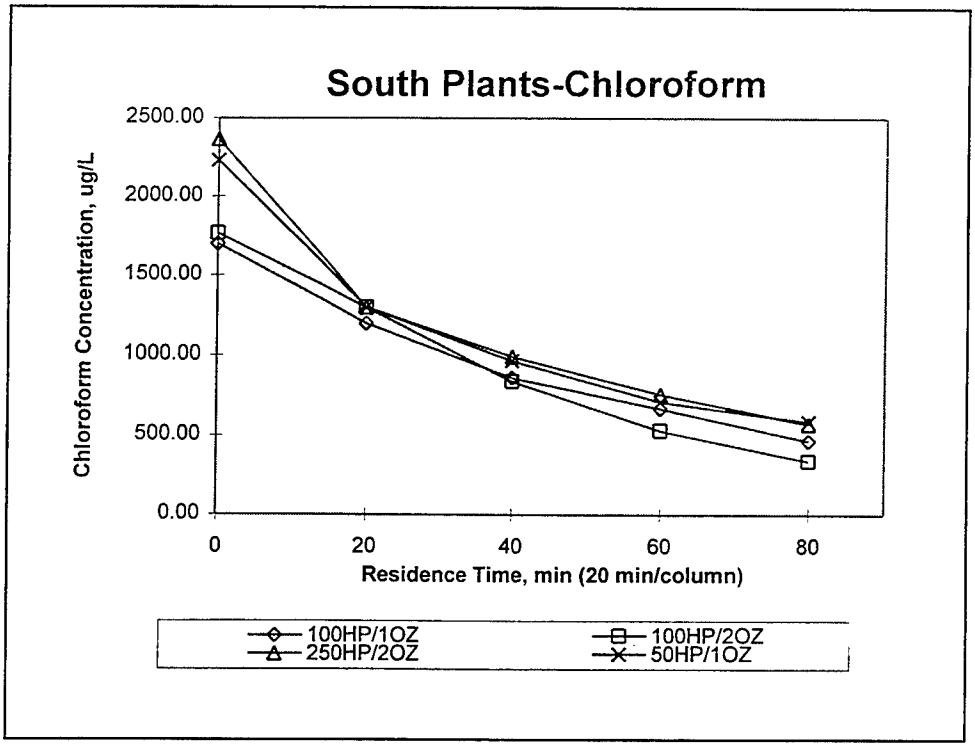

Figure 21. Chloroform removal during SP runs

Trichloroethylene removal

Figure 22 presents the TCE removal data for the SP groundwater. The TCE data indicate that volatilization was the primary mechanism for TCE removal because of the lack of difference noted between the various runs evaluated. All of the systems

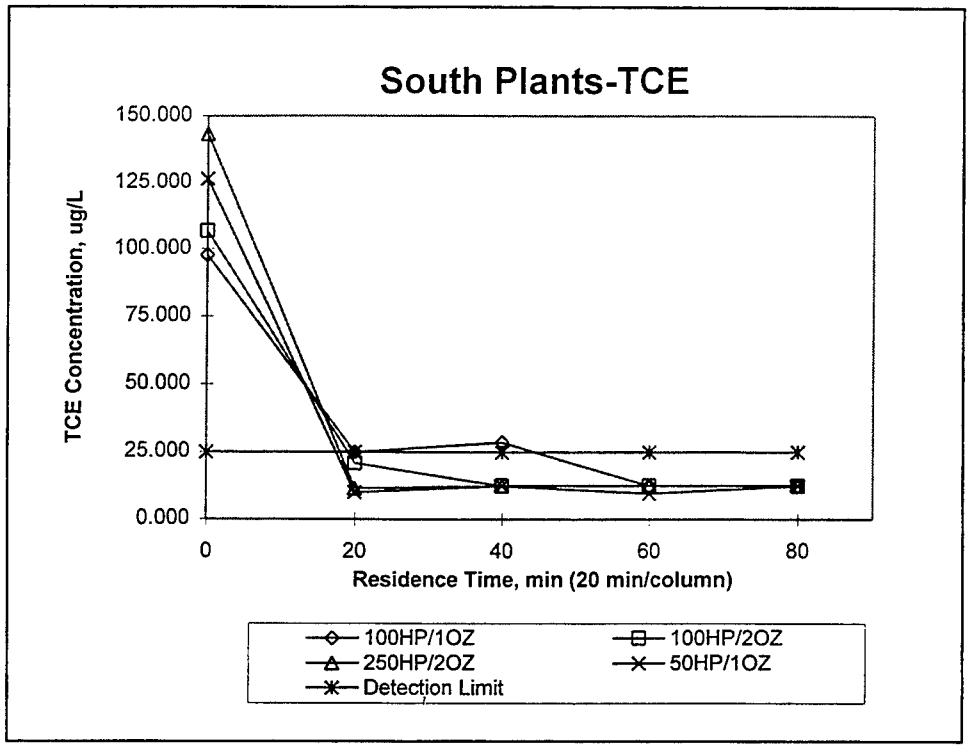

Figure 22. TCE removal during SP runs

except the 100-mg/ℓ hydrogen peroxide, 2-percent ozone-dosed system removed TCE to subdetection limit levels within only 20 min of treatment. The 100-mg/ℓ hydrogen peroxide, 2-percent ozone-dosed system removed TCE to the detection limit value within 20 min; however, the TCE remained at this level until 60 min of treatment when the TCE was removed to subdetection limit values.

Benzene removal

Figure 23 presents the benzene removal data for the SP groundwater. Unlike the TCE and chloroform data, the benzene data indicate slight differences in system performance. Within the first 20 min of treatment, the benzene levels appear to increase except the 100-mg/ℓ hydrogen peroxide, 2-percent ozone system. It is possible that benzene is an intermediate of oxidation of one of the many organic compounds present in the SP groundwater. However, all of the systems except the 100-mg/ℓ hydrogen peroxide, 1-percent ozone-dosed system removed benzene to BDLs within 40 min of treatment. The 100-mg/ℓ hydrogen peroxide, 1-percent ozone system indicated an approximate fourfold increase in benzene levels within the first 20 min of treatment, then removal of benzene to subBDLs within 60 min of treatment.

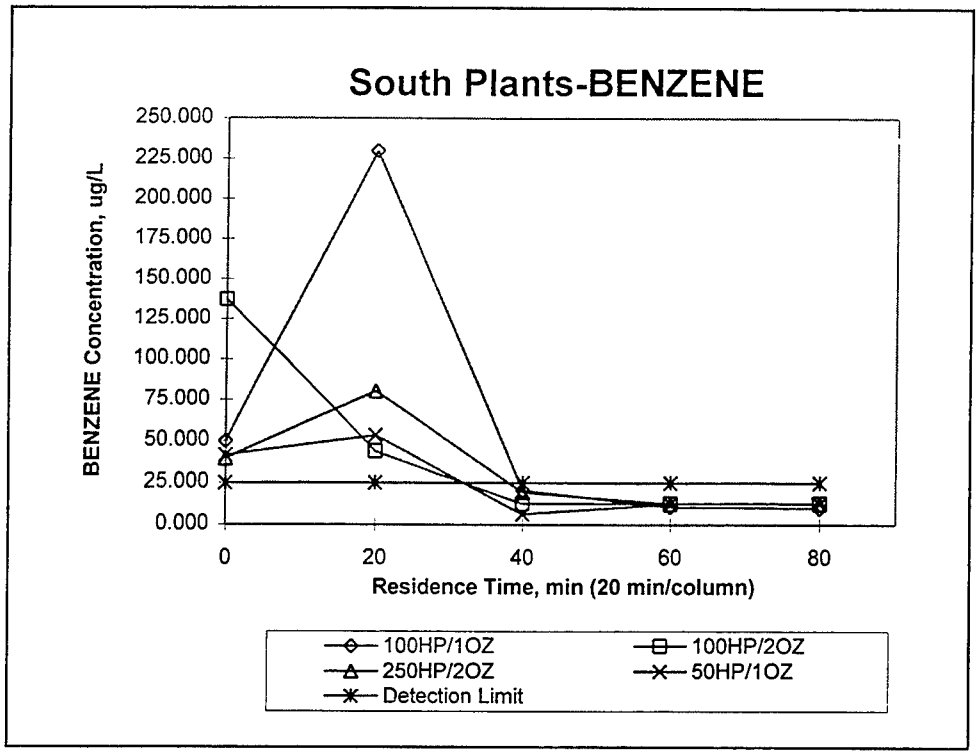

Figure 23. Benzene removal during SP runs

Summary

Table 14 summarizes the results of the SP pilot studies. From this table, it appears that treating the SP groundwater using peroxone may be difficult; however, unlike the BANS groundwater, the potential does exist for peroxone to meet the target treatment goals for the SP groundwater. The 250-mg/ℓ hydrogen peroxide, 2-percent ozone-dosed system was able to meet target levels for all contaminants within an 80-min HRT except for dieldrin, which did show greater than 90-percent removal of dieldrin, which was within 1 percent of meeting the target goal of 0.04 µg/ℓ. The other process systems evaluated did not indicate the same level of potential as did the 250-mg/ℓ hydrogen peroxide-dosed system. The 100-mg/ℓ hydrogen peroxide, 2-percent ozone-dosed system was the next best performer based on the number of ">80 min" appearing under that column in Table 14.

ORP as a Process Control Parameter

Figures 24, 25, and 26 compare selected ORP values and ozone concentrations for selected runs treating NBCS, BANS, and SP groundwaters, respectively. The objective of this comparison was to assess the feasibility of using ORP as a process control parameter.

Table 14
Summary of Required HRTs[1] to Meet the Target Treatment Levels for the SP Experiments

Contaminant	100H/1OZ	100H/2OZ	250H/2OZ	50H/2OZ
Aldrin	>80	>80	<60	<20
Dieldrin	>80	>80	>80	>80
Endrin	>80	<80	<80	ND
$CHCl_3$	>80	>80	>80	>80
TCE	<60	<20	<40	<40
Benzene	ND	<20	<40	<60
Cl-Benzene	ND	<20	<60	ND
Nemagon	>80	>80	ND	>80

Note: H = Hydrogen peroxide; OZ = ozone; ND = not detected in influent.
[1] HRTs in minutes.

From the figures, it appears that ORP nicely tracks with ozone concentration. What is surprising is that when peroxone reactions are occurring (i.e., low ozone and significant quantities of hydrogen peroxide are present) and the oxidation potential toward oxidation of organic constituent is high, that the ORP is low (i.e., approximately 200-300 mV). This observation was quite perplexing while the unit was under operation in the field. However, based on discussion with chemists (Drs. Mohammad Qasim and Andy Hong, WES 1995), it was determined that ORP probes actually measure oxygen coupling. Oxygen couples are present in oxygen species such as ozone and oxygen, but not present in hydrogen peroxide nor hydroxyl radicals. This explains why ORP is low when hydrogen peroxide and/or hydroxyl radicals are present.

In summary, ORP appears to be a good indicator of ozone levels. It can also be used as a rough measure of the level of reduction (i.e., low REDOX) of the influent that the ozone and other oxidants must overcome. A low ORP will serve as a sink if the reductive conditions can be oxidized into a higher ORP. Given the cost and real-time status of ORP probes, it is believed that ORP should remain as a process parameter for future studies with peroxone systems.

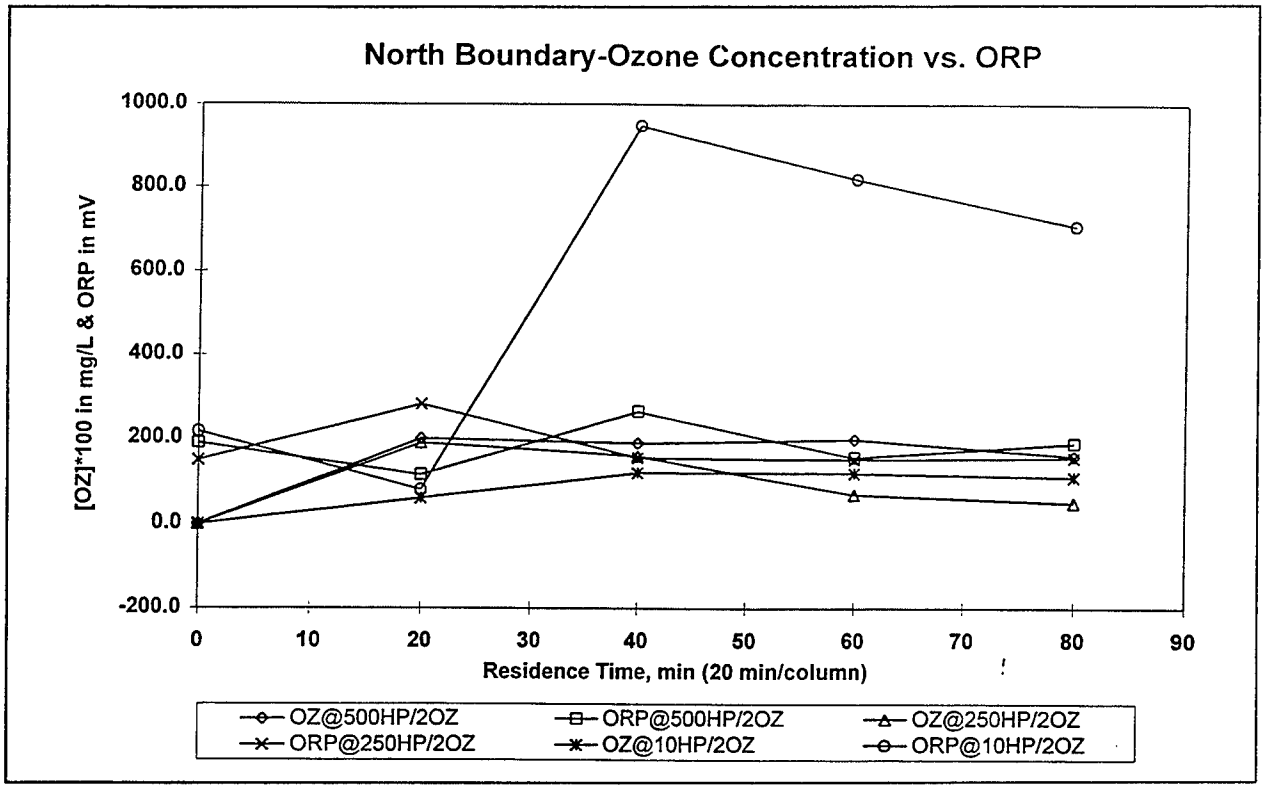

Figure 24. ORP versus ozone concentration for NB runs

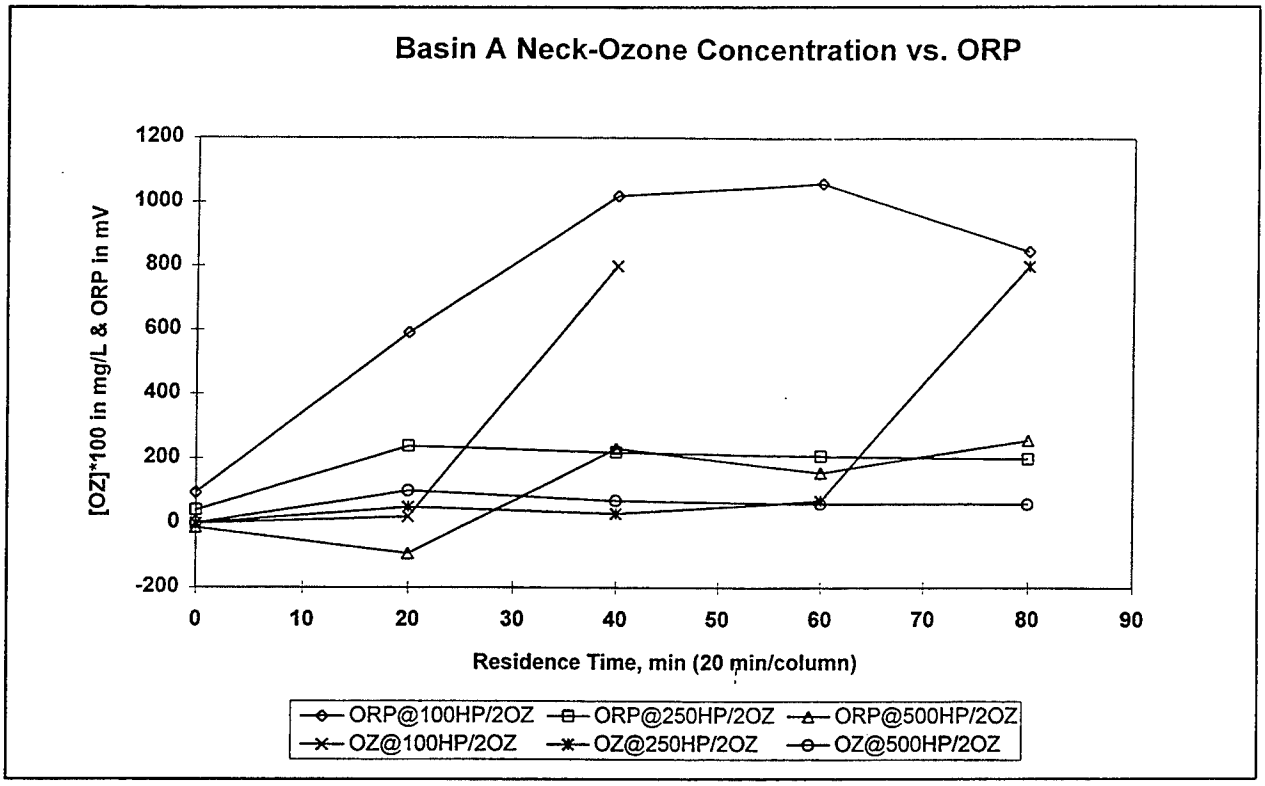

Figure 25. ORP versus ozone concentration for BANS runs

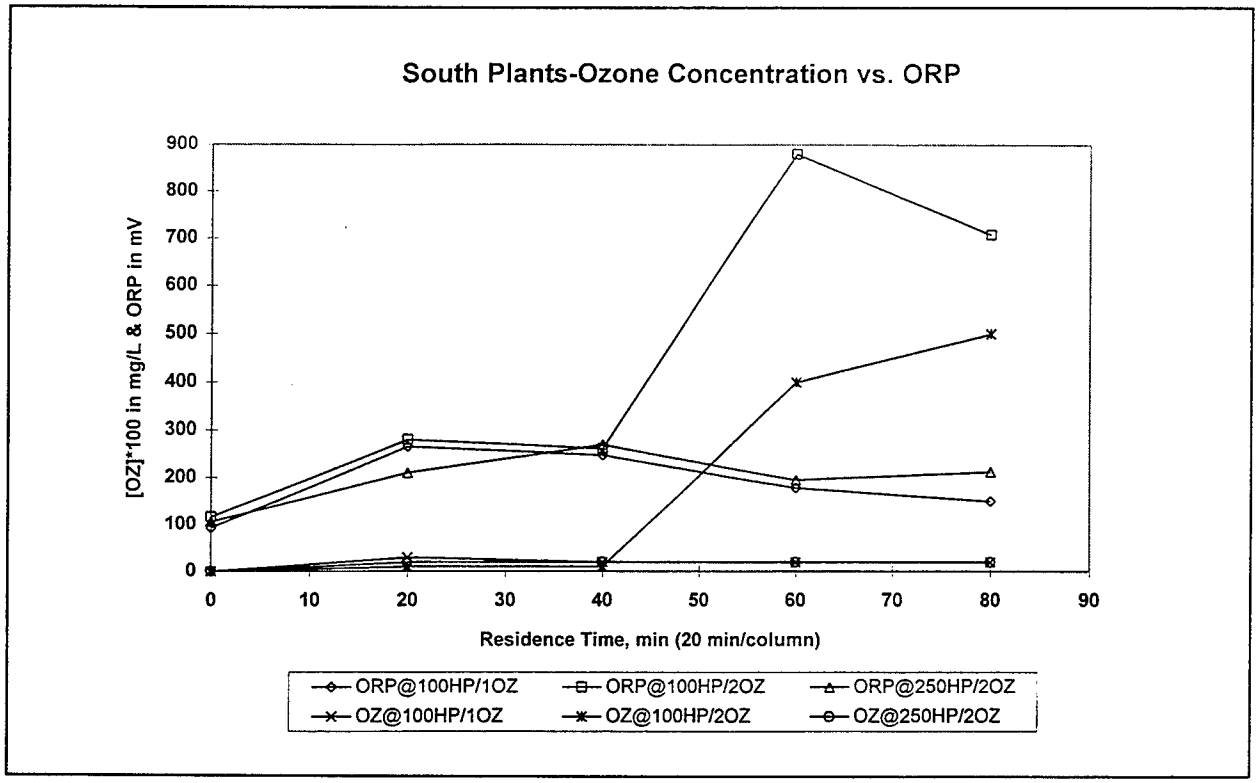

Figure 26. ORP versus ozone concentration for SP runs

5 Conclusions

The results of this study indicate that peroxone was effective for removing targeted contaminants from the NBCS influent. All of the contaminants present in the NBCS influent were removed to levels below the analytical detection limit of the methods used. The 250-mg/ℓ hydrogen peroxide, 2-percent ozone-dosed system was considered the optimal system. This system would require less than 60 min of HRT to reach the target treatment goals.

Peroxone indicated varying degrees of success for removing individual contaminants from the other two test influents studied at RMA. Peroxone was considered ineffective for treatment of the BANS groundwater. The chemical matrix of the BANS groundwater was considered too concentrated in terms of contaminant levels and oxidizer scavengers present. Many of the contaminants in the BANS groundwater that were not removed to BDLs, such as DIMP, NDMA, and chloroform, were removed from the NBCS influent. This observation illustrates how peroxone may work for a group of contaminants in one contaminated water, but fail to adequately perform with another water source if the contaminant and/or scavenger species are present at relatively high levels.

Peroxone did appear to have potential as a treatment option for the SP groundwater. Dieldrin was the only contaminant in the SP groundwater not treated to the target treatment goal of less than detection limit values (0.04 µg/ℓ for dieldrin). As was the case with the NBCS influent, the 250-mg/ℓ hydrogen peroxide, 2-percent ozone-dosed system was also the most promising system evaluated for the SP groundwater. This system required an 80-min HRT to meet the target treatment goals for all of the contaminants except for dieldrin, as opposed to the 60 min-HRT required for the NBCS influent. Dieldrin was reduced to almost target levels (i.e., 0.13 µg/ℓ) using the 250-mg/ℓ hydrogen peroxide, 2-percent ozone-dosed system.

ORP appears to be a useful process control parameter. It does not indicate actual oxidation conditions that are obtainable with peroxone because ORP probes actually measure oxygen coupling. ORP does give good insight into ozone levels and the potential oxidizer demands exerted by incoming waters.

The POPS unit performed well in terms of providing conditions conducive to maintaining peroxone reactions. The ozone automated monitoring system requires

modifications to provide a more rugged system that is less susceptible to high heat conditions.

In general, peroxone appears to be a viable process for removing organic contaminants from contaminated groundwaters. The effectiveness of peroxone is dependent on water chemical matrix and contaminant level.

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Appendix A
Raw Data Sheets

North Boundary (H2O2 100 ppm)

NDMA (ug/L)

Sample	A	B
inlet	0.3	0.365
4	0.11	0.278

DIMP (ug/L)

Sample	A	B
inlet	7.6	7.3
4	6.7	6.6

Volatiles (ug/L)

Sample A	CHCL3	DCPD	TCLEE
Inlet	1.2	9.3	1.2
4	1.6	<1.0	<1.0

System conditions at time samples taken

H2O2 ppm	CHEMetric	RQ Flex	ORP	Flow	pH In	pH Out
Inlet	75	100	216.6	0.9	7.6	8.3
1	60-70	91	-34.4			
2	65-70	71.5	256.3			
3	60-70	67.5	160.5			
4	60-70	82.5	188			

North Boundary (High Flow, Ozone 2%, H2O2 100ppm)

DIMP (ug/L)

Sample	A	B
Inlet	68	<0.87
1	32	3.1
2	13	12.5
3	5.4	4.87
4	<1.78	1.91

Volatiles (ug/L)

Sample A	CHCL3	DCPD	DMDS	TCLEE
Inlet	1.6	10	5.3	1.2
1	2.1	<1.0	1.5	<1.0
2	<1.0	<1.0	<1.0	<1.0
3	2.1	<1.0	<1.0	<1.0
4	>1.0	<1.0	<1.0	<1.0

System conditions at time samples taken

H2O2 ppm	CHEMetric	RQ Flex	ORP	Residual	O3 ppm	Flow	pH In	pH Out	O3 gen %
Inlet	175	118	202.7	1	0.9	2.2	7.8	8.3	2.3
1	150	110.5	303.6	2	0.9				
2	150	108.5	285.4	3	0.6				
3	100	104	188.5	4	0.8				
4	110	90.5	41.8						

North Boundary (Ozone 2%, H2O2 10 ppm)

NDMA (ug/L)

Sample	A
Inlet	0.33
1	0.26
2	0.22
3	0.1
4	0.06

DIMP (ug/L)

Sample	A	B	C
Inlet	74	<.87	<.87
1	43	<.87	----
2	20	----	18
3	10	8.43	8.32
4	5.8	4.32	----

Pesticides (ug/L)

Sample A	DIELDRIN	ENDOII	ENDRIN	NEMAGON	ALDRIN	PPDDD
Inlet	0.3	0.42	0.18	0.03	0.06	0.16
1	0.23	0.35	0.15	0.05	LOST	LOST
2	LOST	LOST	LOST	LOST	<.040	0.12
3	0.11	<.040	0.09	<.050	<.040	0.05
4	0.16	<.040	<.060	<.050	<.040	<.11

Sample B	DIELDRIN	ENDOII	ENDRIN	NEMAGON	ALDRIN	PPDDD
Inlet	0.21	<.040	<.060	<.050	<.040	0.05
1	0.33	<.040	<.060	<.050	<.040	<.11
2	0.26	<.040	<.060	<.050	<.040	<.11
3	0.19	<.040	<.060	<.050	<.040	<.11
4	0.13	<.040	<.060	<.050	<.040	<.11

Sample C	DIELDRIN	ENDOII	ENDRIN	NEMAGON	ALDRIN	PPDDD
inlet	0.2	<.040	<.060	<.050	<.040	0.03
1	0.11	<.040	<.060	<.050	<.040	<.11
2	LOST	LOST	LOST	LOST	LOST	LOST
3	LOST	LOST	LOST	LOST	LOST	LOST
4	LOST	LOST	LOST	LOST	LOST	LOST

*BDL-below detection limit

Volatiles (ug/L)

Sample A	CHCL3	DCPB	TCLEE
Inlet	2	8.7	1.2
1	1.3	<1.0	<1.0
2	1.9	<1.0	<1.0
3	1.1	<1.0	<1.0
4	<1.0	<1.0	<1.0

System conditions at time samples taken

H2O2	CHEMetric	Residual	O3 ppm	ORP	
inlet	10	1	0.6	Inlet	217
1	0.5	2	1.2	1	<80
2	<.5	3	1.2	2	948
3	<.5	4	1.1	3	820
4	<.5			4	708

Flow	pH In	pH Out
0.8gpm	7.6	8.3

North Boundary (Ozone 2%, H2O2 100 ppm)

NDMA (ug/L)

Sample	A	B
inlet	0.321	0.327
1	0.327	0.276
2	0.083	0.1
3	0.016	0.021
4	0.006	0.007

DIMP (ug/L)

Sample	A	B	C
inlet	77	66	74
1	14	13	16
2	<1.78	<1.78	<1.78
3	<1.78	<1.78	<1.78
4	<1.78	<1.78	<1.78

*BDL-below detection limit

System conditions at time samples taken

H2O2ppm	CHEMetric	ORP	
1	100	1	285
2	50	2	259
3	0.3	3	937
4	0.2	4	486

Flow	pH In	pH Out
.84gpm	7.58	8.23

Pesticides (ug/L)

Sample A	ALDRIN	PPDDD	HPTCL	DIELDRIN	ENDOII	ENDRIN	ENDALD
Inlet	0.12	0.18	<.033	0.35	0.49	0.21	<.25
1	<.045	0.04	<.034	0.19	<.045	0.24	7.4
2	<.044	<.12	<.033	<.022	<.044	0.1	<.26
3	<.047	<.13	<.035	0.01	<.047	<.071	<.27
4	<.047	<.13	<.035	<.024	<.047	<.071	<.27

Sample B	ALDRIN	PPDDD	HPTCL	DIELDRIN	ENDOII	ENDRIN	ENDALD
Inlet	0.03	0.08	0.13	0.69	0.08	0.23	0.14
1	<.047	0.05	<.035	<.024	<.047	0.15	<.27
2	<.045	<.13	<.034	<.023	<.045	0.06	<.26
3	<.043	<.12	<.032	<.021	<.043	<.064	<.24
4	<.043	<.12	<.032	<.021	<.043	<.064	<.24

Sample C	ALDRIN	PPDDD	HPTCL	DIELDRIN	ENDOII	ENDRIN	ENDALD
Inlet	0.09	0.1	<.031	0.63	0.18	0.21	0.11
1	<.046	0.04	<.034	0.19	<.046	0.15	0.04
2	<.044	<.12	<.033	<.022	<.044	0.05	<.25
3	<.043	<.12	<.032	<.022	<.043	<.065	<.25
4	<.044	<.12	<.033	<.022	<.044	<.066	<.25

North Boundary (Ozone 2.4%, H2O2 100 ppm)

NDMA (ug/L)

Sample	A	B
inlet	0.24	0.368
4	0.012	0.036

DIMP (ug/L)

Sample	A	B
inlet	76	76
4	<1.78	<1.78

Pesticides (ug/L)

Sample A	ALDRIN	HPTCL	PPDDD	DIELDRIN	ENDOII	ENDRIN
inlet	0.09	0.04	0.2	0.39	0.52	0.2
4	BDL	BDL	BDL	0.04	BDL	BDL

Sample B	ALDRIN	HPTCL	PPDDD	DIELDRIN	ENDOII	ENDRIN
inlet	BDL	BDL	0.18	0.37	0.49	0.19
4	BDL	BDL	BDL	0.04	BDL	BDL

Volatiles (ug/L)

Sample A	CHCL3	DCPD	TCLEE
Inlet	1.1	9	1.2
4	<1.0	<1.0	<1.0

*BDL-below detection limit

System conditions at time samples taken

H2O2 ppm	CHEMetric	RQ Flex	Residual	O3 ppm	ORP	
inlet	175	118	inlet	—	inlet	208
1	150	110.5	1	0.9	1	310
2	150	108.5	2	0.9	2	293
3	100	104	3	0.6	3	194
4	110	90.5	4	0.8	4	135

Flow	pH In	pH Out	O3 gen %
2.2gpm	7.7	8.2	2.3

North Boundary (Ozone 2%, H2O2 250 ppm)

NDMA (ug/L)

Sample	A
inlet	0.29
1	0.38
2	0.14
3	<.012
4	<.012

DIMP (ug/L)

Sample	A	B	C
inlet	9.6	65	5.7
1	10	9.9	10
2	<1.78	<1.78	1.51
3	<1.78	<1.78	<.87
4	<1.78	<1.78	<.87

Pesticides (ug/L)

Sample A	DIELDRIN	NEMAGON
Inlet	LOST	LOST
1	LOST	LOST
2	0.04	<.05
3	0.58	26
4	0.33	18

Volatiles (ug/L)

Sample B	CHCL3	DCPD	TCLEE
Inlet	2.1	6.9	1.1
1	<1.0	<1.0	<1.0
2	<1.0	<1.0	<1.0
3	<1.0	<1.0	<1.0
4	<1.0	<1.0	<1.0

Sample C	CHCL3
Inlet	<100
1	<50
2	9.3
3	LOST
4	LOST

*BDL-below detection limit

System conditions at time samples taken

H2O2 ppm	CHEMetric	Residual	O3 ppm
1	200	1	1.9
2	125	2	1.6
3	75	3	0.7
4	<50	4	0.5

ORP	
Inlet	149.2
1	281.7
2	155
3	152.3
4	156.2

Flow	pH In	pH Out	O3 gen %
0.9	7.5	8.3	2.1

North Boundary (Ozone 2-2.5%, H2O2 500 ppm)

NDMA (ug/L)

Sample	A	B
inlet	0.26	0.28
1	0.69	0.69
2	0.39	0.35
3	0.21	0.22
4	0.089	0.086

Dimp (ug/L)

Sample	A	B	C
inlet	145	56	----
1	<1.78	13	17.9
2	<1.78	3.7	4.89
3	<1.78	<1.78	1.14
4	<1.78	<1.78	0.87

Pesticides (ug/L)

Sample A	PPDDD	HPTCL	DIELDRIN	ENDOII	ENDRIN
inlet	0.09	<.031	0.1	<.041	0.08
1	0.13	<.037	<.025	<.049	0.1
2	0.06	<.035	0.06	<.047	0.06
3	<.14	<.038	<.025	<.05	0.04
4	<.12	<.033	<.022	<.043	0.03

Sample B	PPDDD	HPTCL	DIELDRIN	ENDOII	ENDRIN
inlet	0.18	0.05	0.31	0.46	0.18
1	0.09	<.032	0.12	<.043	0.12
2	<.12	<.033	<.022	<.044	0.03
3	0.06	<.034	<.022	<.045	0.1
4	<.12	<.035	<.024	<.047	0.01

Sample C	PPDDD	HPTCL	DIELDRIN	ENDOII	ENDRIN
inlet	LOST	LOST	LOST	LOST	LOST
1	0.24	0.05	0.41	0.6	0.24
2	0.05	<.032	<.021	<.043	0.06
3	<.13	<.036	<.024	<.048	0.03
4	<.13	<.035	<.023	<.047	<.07

*BDL-below detection limit

System conditions at time samples taken

H2O2 ppm	CHEMetric	Residual	O3 ppm	ORP	
1	500	1	2	Inlet	190
2	350	2	1.9	1	115
3	275	3	2	2	265
4	200	4	1.6	3	157
				4	190

Flow	pH In	pH Out
.8gpm	7.7	8.3

Volatiles (ug/L)

Sample C	12DCLE	BCHPD	CH2CL2	CHCL3	DCPD	TCLEE	TRCLE
Inlet	25	11	6.8	120	112	41	12
1	17	<1.0	4	>100	<1.0	2.6	<1.0
2	12	<1.0	12	>100	<1.0	<1.0	<1.0
3	11	<1.0	9.4	>100	<1.0	<1.0	<1.0
4	8.8	<1.0	5.8	>100	<1.0	<1.0	<1.0

Basin A (Ozone 1%, H2O2 50 ppm)

NDMA (ug/L)

Sample	A	B
Inlet	2.2	3.7
2	3	2.7
4	----	2.8

DIMP (ug/L)

Sample	A	B	C
Inlet	898	900	921
1	803	788	791
2	725	716	725
3	647	612	594
4	538	543	559

Volatiles (ug/L)

Sample A	12DCLE	CH2CL2	CHCL3	DCPD	TCLEE
Inlet	15	19	>1000	29	15
1	13	16	>1000	<1	<1
2	12	14	>1000	<1	<1
3	<2	12	>1000	<1	<1
4	<2	12	510	<1	<1

Sample C	12DCLE	CH2CL2	CHCL3	DCPD	TCLEE
Inlet	<2	<1	>1000	25	14
1	13	14	>1000	<1	<1
2	12	13	>1000	<1	<1
3	<2	10	>1000	<1	<1
4	<2	<1	510	<1	<1

Sample B	12DCLE	CH2CL2	CHCL3	DCPD	TCLEE
Inlet	15	18	>1000	38	17
1	11	15	>1000	<1	<1
2	12	15	>1000	<1	<1
3	<2	12	>1000	<1	<1
4	<2	<1	500	<1	<1

System conditions at time samples taken

H2O2 ppm	CHEMetric	RQ Flex	Residual	O3 ppm
Inlet	50	50	Inlet	----
1	40	56	1	0.2
2	30-35	44	2	0.2
3	5	4.7	3	1.2
4	5	4.4	4	8

Flow	pH In	pH Out	O3 gen %
.863gpm	7.2	7.5	1.09

Basin A (Ozone 1%, H2O2 100 ppm)

Volatiles (ug/L)

Sample A	12DCLE	CHCL3	DCPD	TCLEE	CH2CL2
Inlet	18	>1000	42	20	<1
1	18	>1000	<1	<1	14
2	13	>1000	<1	<1	13
3	10	>1000	<1	<1	10
4	<2	>1000	<1	<1	<1

Sample B	12DCLE	CHCL3	DCPD	TCLEE	CH2CL2
Inlet	14	>1000	30	16	16
1	14	>1000	<1	<1	14
2	14	>1000	<1	<1	14
3	<2	>1000	<1	<1	<1
4	<2	>1000	<1	<1	<1

Sample C	12DCLE	CHCL3	DCPD	TCLEE	CH2CL2
Inlet	19	>1000	33	18	21
1	15	>1000	<1	<1	<1
2	13	>1000	<1	<1	17
3	10	>1000	<1	<1	<1
4	<2	>1000	<1	<1	12

NDMA (ug/L)

Sample	A	C
Inlet	2.4	2.3
2	2.7	2.8
4	2.3	2.4

System conditions at time samples taken

H2O2 ppm	CHEMetric	RQ Flex	Residual	O3 ppm
Inlet	100	----	Inlet	----
1	90	89	1	0.8
2	90	22.8	2	0.6
3	65	24.5	3	0.6
4	50	----	4	0.8

Flow	pH In	pH Out	O3 gen %
.857gpm	7.33	7.91	1.02

Basin A (Ozone 2%, H2O2 100 ppm)

Volatiles (ug/L)

Sample A	12DCLE	BCHPD	BENZENE	CH2CL2	CHCL3	CHBR3	DCPD	TCLEE	TRCLE	DBRCLM	DMDS
Inlet	21	9.5	5.7	5.9	>100	<1.0	>100	45	12	<1.0	<1.0
1	7.4	<1.0	<1.0	4.1	>100	6.6	<1.0	<1.0	<1.0	<1.0	<1.0
2	8.3	<1.0	1.1	5.9	>100	3	<1.0	2	1.2	<1.0	<1.0
3	5.9	<1.0	<1.0	<1.0	>100	32	<1.0	<1.0	<1.0	3.6	<1.0
4	6.3	<1.0	<1.0	2.3	>100	39	<1.0	<1.0	<1.0	12	<1.0

Sample B	12DCLE	BCHPD	BENZENE	CH2CL2	CHCL3	CHBR3	DCPD	TCLEE	TRCLE	DBRCLM	DMDS
Inlet	21	8.4	5.3	27	>100	<1.0	>100	37	11	<1.0	<1.0
1	8.2	<1.0	<1.0	1.9	>100	7.2	<1.0	<1.0	<1.0	<1.0	<1.0
2	7.4	<1.0	<1.0	1.3	>100	2.9	<1.0	1.7	<1.0	<1.0	1.1
3	6.2	<1.0	<1.0	2.8	>100	37	<1.0	<1.0	<1.0	5.8	2.7
4	5.4	<1.0	<1.0	<1.0	>100	37	<1.0	<1.0	<1.0	13	2.7

Sample C	12DCLE	BCHPD	BENZENE	CH2CL2	CHCL3	CHBR3	DCPD	TCLEE	TRCLE	DBRCLM	DMDS
Inlet	20	9.4	5.3	24	>100	<1.0	>100	44	12	<1.0	<1.0
1	7.6	<1.0	<1.0	3.4	>100	6.5	<1.0	<1.0	<1.0	<1.0	<1.0
2	9.9	<1.0	<1.0	6.5	>100	3.8	<1.0	2	1.1	<1.0	1.9
3	6.4	<1.0	<1.0	2.3	>100	35	<1.0	<1.0	<1.0	11	1.8
4	5.7	<1.0	<1.0	2	>100	38	<1.0	<1.0	<1.0	11	<1.0

System conditions at time samples taken

H2O2 ppm	CHEMetric	RQ Flex	ORP	Residual	O3 ppm
Inlet	75	79	94	Inlet	0
1	40	40.5	592	1	0.2
2	10	3	1020	2	8
3	10	10	1060	3	----
4	20	15.5	847	4	----

pH In	pH Out	Flow	O3 gen%
1.7	1.7	0.9	2.1

NDMA (ug/L)

Sample	A	B
Inlet	2.852	1.7
1	6.16	10
2	5.606	10
3	6.355	3.7
4	4.773	8

DIMP (ug/L)

Sample	A	B	C
Inlet	644	629	872
1	722	615	837
2	704	600	723
3	611	610	701
4	637	619	694

Basin A (Ozone 2%, H2O2 250 ppm)

NDMA (ug/L)

Sample	A	C
Inlet	2.1	2
1	----	----
2	3.9	2.1
3	----	----
4	3	3.1

DIMP (ug/L)

Sample	A	B	C
Inlet	7.7	948	871
1	5.6	608	628
2	3.5	375	382
3	2.1	250	244
4	1.9	217	225

Volatiles (ug/L)

Sample A	12DCLE	CH2CL2	DCPD	TCLEE	CHCL3
Inlet	17	19	46	19	>1000
1	13	15	<1.0	<1.0	>1000
2	<2.0	13	<10	<1.0	>1000
3	<2.0	<1.0	<10	<1.0	>1000
4	<2.0	13	<10	<1.0	760

Sample B	12DCLE	CH2CL2	DCPD	TCLEE	CHCL3
Inlet	16	21	40	20	>1000
1	13	19	<10	<1	>1000
2	<2	15	<10	<1	>1000
3	<2	14	<10	<1	>1000
4	<2	13	<10	<1	700

Sample C	12DCLE	CH2CL2	DCPD	TCLEE	CHCL3
Inlet	18	18	41	19	>1000
1	13	18	<10	<1	>1000
2	11	17	<10	<1	>1000
3	<2	14	<10	<1	>1000
4	<2	13	<10	<1	720

System conditions at time samples taken

H2O2 ppm	CHEMetric	RQ Flex	ORP	Residual	O3 ppm
Inlet	250	----	40	Inlet	----
1	150	124	238	1	0.5
2	100	70	219	2	0.3
3	15	14	207	3	0.7
4	0	2	200	4	>8.0

pH In	pH Out	Flow	O3 gen%
7.12	7.91	0.9	2.2

Basin A (Ozone 2%, H2O2 500 ppm)

Volatiles (ug/L)

Sample A	12DCLE	CH2CL2	CHCL3	DCPD	TCLEE
Inlet	16	21	>1000	36	18
1	12	18	>1000	<10	<1
2	11	27	>1000	<1	<1
3	<2	10	>1000	<1	<1
4	<2	<1	>1000	<1	<1

Sample B	12DCLE	CH2CL2	CHCL3	DCPD	TCLEE
Inlet	20	19	>1000	41	23
1	16	16	>1000	<1	<1
2	12	12	>1000	<1	<1
3	<2	10	>1000	<1	<1
4	<2	<1	>1000	<1	<1

DIMP (ug/L)

Sample	A	B	C
Inlet	8.4	875	891
1	5	620	585
2	3.1	362	357
3	17	197	210
4	1.1	122	----

System conditions at time samples taken

H2O2 ppm	CHEMetric	RQ Flex	ORP	Residual	O3 ppm	Flow	pH In	pH Out	O3 gen %
Inlet	500	----	-12.6	1	1	0.9	6.7	7.4	2.2
1	400	256	-94.1	2	0.7				
2	300	188	231	3	0.6				
3	275	170	156.2	4	0.6				
4	200	90	257.5						

South Plants (No Ozone, No H2O2)

Pesticides (ug/L)

Sample A	ALDRIN	A-BHC	DIELDRIN	HPTCL	ENDRIN	NEMAGON
Inlet	0.41	<.030	3.6	0.03	<.060	120
1	0.26	<.030	3.3	0.03	<.060	120
2	0.21	<.030	3.2	<.030	<.060	120
3	0.17	<.030	3.3	<.030	<.060	120
4	0.12	<.030	3	0.03	<.060	110

Sample B	ALDRIN	A-BHC	DIELDRIN	HPTCL	ENDRIN	NEMAGON
Inlet	0.45	<.030	3.6	0.04	<.060	120
1	0.24	<.030	3	0.03	<.060	110
2	0.22	<.030	3.2	<.030	<.060	120
3	0.17	<.030	3	<.030	2.6	110
4	0.14	<.030	3.2	<.030	<.060	110

Sample C	ALDRIN	A-BHC	DIELDRIN	HPTCL	ENDRIN	NEMAGON
Inlet	0.45	0.26	3.6	<.030	2.7	120
1	0.25	<.030	3.2	<.030	2.7	110
2	0.2	<.030	3.1	<.030	<.060	120
3	0.15	<.030	3.2	<.030	<.060	120
4	0.12	<.030	3.1	<.030	<.060	110

Volatiles (ug/L)

Sample A	CHCL3	TCE
Inlet	2000	110
1	1400	20
2	1000	22
3	LOST	LOST
4	LOST	LOST

Sample B	CHCL3	TCE
Inlet	2200	120
1	1300	41
2	1000	22
3	800	72
4	LOST	LOST

Sample C	CHCL3	TCE
Inlet	LOST	LOST
1	LOST	LOST
2	LOST	LOST
3	LOST	LOST
4	LOST	LOST

***BDL-below detection limit**

HNU readings

Influent Tank <1 ppm
Column 1 off-gas 49 ppm
Column 1 off-gas after GAC 0 ppm
Columns 2,3,4 off-gas 14 ppm
Columns 2,3,4 off-gas after GAC 0 ppm

ORP		pH In	pH Out	Flow
Inlet	103	7.6	8.3	0.8
1	201			
2	215			
3	156			
4	148			

South Plants (Ozone 1%, H2O2 50 ppm)

Pesticides (ug/L)

Sample A	ALDRIN	A-BHC	DIELDRIN	ENDRIN	ENDALD	NEMAGON
Inlet	0.42	<.030	3.8	<.060	<.23	120
1	<.040	<.030	2.6	<.060	<.23	98
2	<.040	<.030	1.9	<.060	<.23	87
3	<.040	0.13	1.5	<.060	<.23	75
4	<.040	0.11	1.2	<.060	<.23	63

Sample B	ALDRIN	A-BHC	DIELDRIN	ENDRIN	ENDALD	NEMAGON
Inlet	0.38	0.24	3.7	<.060	<.23	110
1	<.040	0.19	2.5	<.060	<.23	98
2	<.040	0.17	2	<.060	<.23	87
3	<.040	0.13	1.5	<.060	<.23	75
4	<.040	0.11	1.1	<.060	0.23	62

Sample C	ALDRIN	A-BHC	DIELDRIN	ENDRIN	ENDALD	NEMAGON
Inlet	<.040	0.11	1.2	<.060	<.23	62
1	<.040	0.13	1.5	1	<.23	74
2	<.040	0.16	1.9	1.4	<.23	86
3	<.040	0.2	2.5	1.8	<.23	100
4	0.44	0.29	3.8	2.6	<.23	120

*BDL-below detection limit

Volatiles (ug/L)

Sample A	CHCL3	BrDCIME	TCE	BENZENE	CIBEN
Inlet	800	<50	49	<50	<50
1	1300	<50	14	70	<50
2	960	<25	<25	4.9	<25
3	730	<25	<25	<25	<25
4	560	<25	<25	<25	<25

Sample B	CHCL3	BrDCIME	TCE	BENZENE	CIBEN
Inlet	3900	<100	220	<100	<100
1	1300	<50	7.9	65	180
2	950	<25	<25	7.2	22
3	710	<25	3.6	<25	2.8
4	560	<25	<25	<25	<25

Sample C	CHCL3	BrDCIME	TCE	BENZENE	CIBEN
Inlet	2000	<100	110	<100	<100
1	1300	<50	8.2	<50	200
2	1000	3.4	<25	7.1	23
3	700	2.7	<25	<25	2.7
4	650	<25	<25	<25	<25

System conditions at time samples taken

H2O2 ppm	CHEMetric	RQ Flex	ORP	Residual	O3 ppm
Inlet	50	51	107.2	Inlet	----
1	40	33.5	-327.1	1	0.2
2	25	27	253.3	2	0.1
3	15	13	183.5	3	0.3
4	7	4	159	4	0.2

Flow	pH In	pH Out	O3 gen %
.85gpm	7.67	8.01	1

South Plants (Ozone 1%, H2O2 100 ppm)

Pesticides (ug/L)

Sample A	ALDRIN	A-BHC	B-BHC	G-BHC	PPDDD	PPDDT	HPTCL	DIELDRIN	ENDOII	ENDRIN	ENDALD	HPTCLE	NEMAGON
Inlet	0.53	0.11	0.4	0.11	0.39	0.18	0.09	4.4	1.4	0.91	0.37	BDL	48
1	0.07	0.06	0.28	0.02	0.33	0.14	0.53	3.4	1.2	0.91	0.27	BDL	43
2	0.09	0.04	0.38	0.01	0.3	0.12	0.53	3	1.1	0.68	0.23	BDL	42
3	0.08	0.04	0.39	<.040	0.24	0.09	0.31	2.2	0.89	0.55	BDL	BDL	37
4	0.04	0.02	0.18	<.040	0.17	<.12	<.030	1.6	BDL	0.35	0.31	BDL	31

Sample B	ALDRIN	A-BHC	B-BHC	G-BHC	PPDDD	PPDDT	HPTCL	DIELDRIN	ENDOII	ENDRIN	ENDALD	HPTCLE	NEMAGON
Inlet	0.72	0.18	0.45	0.16	0.44	0.17	0.18	4.8	1.5	1.3	0.47	0.66	33
1	0.36	0.1	0.48	0.11	0.43	0.19	0.56	3.7	1.3	1.1	0.41	BDL	42
2	0.28	0.06	0.59	0.05	0.35	0.14	0.56	3.1	1.2	0.83	0.31	BDL	39
3	0.27	0.04	0.44	<.040	0.27	0.1	<.030	2.2	0.92	0.59	0.23	BDL	34
4	0.18	0.02	0.31	<.040	0.18	0.06	<.030	1.7	BDL	0.36	BDL	BDL	30

Sample C	ALDRIN	A-BHC	B-BHC	G-BHC	PPDDD	PPDDT	HPTCL	DIELDRIN	ENDOII	ENDRIN	ENDALD	HPTCLE	NEMAGON
Inlet	LOST	LOST	LOST	LOST	LOST	LOST	LOST	LOST	----	----	----	BDL	----
1	0.24	0.07	0.3	0.02	0.35	0.14	0.54	3.6	1.2	0.97	0.29	BDL	42
2	0.18	0.04	0.37	0.01	0.29	0.11	0.53	2.9	1	0.68	BDL	BDL	39
3	0.25	0.03	0.25	<.040	0.25	<.12	<.030	2.2	0.89	0.51	0.23	BDL	35
4	0.21	0.02	0.22	<.040	0.17	0.06	<.030	1.7	BDL	0.35	BDL	BDL	29

Volatiles (ug/L)

Sample A	CHCL3	TCE	BENZENE	CIBEN
Inlet	1800	100	<100	<100
1	1300	28	260	450
2	910	32	<25	65
3	670	<25	<25	79
4	510	<25	<25	<25

Sample B	CHCL3	TCE	BENZENE	CIBEN
Inlet	1600	93	<100	<100
1	1100	25	220	450
2	800	28	23	53
3	660	<25	<25	14
4	450	<25	<25	<25

Sample C	CHCL3	TCE	BENZENE	CIBEN
Inlet	1700	100	<100	<100
1	1200	22	210	430
2	880	26	26	64
3	680	<25	7.2	17
4	450	<25	4.8	4.6

*BDL-below detection limit

System conditions at time samples taken

H2O2 ppm	CHEMetric	RQ Flex	ORP	Residual	O3 ppm
Inlet	100	75	93	Inlet	----
1	100	65	266	1	0.3
2	65	55	248	2	0.2
3	50	50	179	3	0.2
4	50	43	150	4	0.2

Flow	pH In	pH Out	O3 gen %
0.847	7.59	8.17	1.01

HNU readings

Influent Tank 2 ppm
Column 1 off-gas 40 ppm
Column 1 off-gas after GAC 0.5 ppm
Columns 2,3,4 off-gas 2.5 ppm
Columns 2,3,4 off-gas after GAC 0 ppm

South Plants (Ozone 2%, H2O2 100 ppm)

Pesticides (ug/L)

Sample A	ALDRIN	A-BHC	B-BHC	G-BHC	PPDDD	PPDDT	HPTCL	DIELDRIN	ENDOII	ENDRIN	ENDALD	NEMAGON
Inlet	0.4	0.1	0.38	0.11	0.37	0.17	0.12	2.9	1.3	1	0.34	46
1	0.1	0.03	0.3	<.040	0.24	0.08	0.45	1.9	0.87	0.53	0.19	38
2	0.03	0.02	0.24	<.040	0.13	<.12	<.030	0.99	<.040	0.27	<.23	26
3	0.09	<.030	0.07	<.040	0.04	<.12	<.030	0.45	<.040	0.15	<.23	15
4	0.11	<.030	<.06	<.040	0.02	<.12	<.030	0.27	<.040	<.050	<.23	10

Sample B	ALDRIN	A-BHC	B-BHC	G-BHC	PPDDD	PPDDT	HPTCL	DIELDRIN	ENDOII	ENDRIN	ENDALD	NEMAGON
Inlet	0.48	0.1	0.41	0.11	0.39	0.18	0.08	3.1	1.3	1.1	0.37	50
1	0.04	0.03	0.32	<.040	0.15	0.06	0.37	1.1	0.53	0.33	0.11	25
2	0.13	<.030	0.24	<.040	0.12	<.12	0.15	0.96	<.040	0.28	0.17	25
3	LOST	LOST	LOST	LOST	LOST	LOST	LOST	LOST	LOST	LOST	LOST	LOST
4	0.02	<.030	<.06	<.040	0.03	<.12	<.030	0.35	<.040	0.05	<.23	11

Sample C	ALDRIN	A-BHC	B-BHC	G-BHC	PPDDD	PPDDT	HPTCL	DIELDRIN	ENDOII	ENDRIN	ENDALD	NEMAGON
Inlet	0.49	0.11	0.42	0.12	0.41	0.18	0.1	3.2	1.4	1.1	0.41	52
1	0.05	0.03	0.32	<.040	0.25	0.09	0.49	1.9	0.86	0.57	0.19	38
2	0.07	0.02	0.26	<.040	0.13	<.12	<.030	0.81	<.040	0.3	0.18	25
3	0.11	<.030	0.07	<.040	0.05	<.12	<.030	0.45	<.040	0.16	0.06	15
4	0.16	<.030	<.06	<.040	0.03	<.12	<.030	0.34	<.040	0.06	<.23	12

Volatiles (ug/L)

Sample A	MECL	CHCL3	TCE	BENZNE	CIBEN
Inlet	42	1800	110	290	2100
1	61	1300	<50	54	99
2	19	830	<25	<25	<25
3	18	520	<25	<25	<25
4	18	340	<25	<25	<25

Sample B	MECL	CHCL3	TCE	BENZNE	CIBEN
Inlet	170	1800	110	110	1800
1	51	1300	<50	52	<50
2	18	840	<25	<25	<25
3	19	530	<25	<25	<25
4	18	340	<25	<25	<25

Sample C	MECL	CHCL3	TCE	BENZNE	CIBEN
Inlet	71	1700	100	12	<100
1	19	1300	<25	<50	<50
2	23	850	<25	<25	32
3	18	550	<25	<25	<25
4	16	350	<25	<25	<25

*BDL-below detection limit

System conditions at time samples taken

H2O2 ppm	CHEMetric	RQ Flex	ORP	Residual	O3 ppm
Inlet	100	97.5	116	Inlet	----
1	65	51	280	1	0.1
2	20	25	262	2	0.1
3	2.5	1	880	3	4
4	0	1	708	4	5

Flow	pH In	pH Out	O3 gen %
.82gpm	7.6	8.04	2.2

HNU readings

Influent Tank 30 ppm
Column 1 off-gas 32 ppm
Column 1 off-gas after GAC <1 ppm
Columns 2,3,4 off-gas after GAC <1 ppm
Effluent Tank 0 ppm

South Plants (Ozone 2%, H2O2 250 ppm)

Pesticides (ug/L)

Sample A	ALDRIN	A-BHC	B-BHC	G-BHC	PPDDD	PPDDT	HPTCL	DIELDRIN	ENDOII	ENDRIN	ENDALD	HPTCLE	NEMAGON
Inlet	0.65	0.13	0.5	0.17	0.45	0.21	0.17	4	1.5	1.2	0.51	0.76	45
1	0.21	0.05	0.35	0.01	0.31	0.12	0.54	2.7	1	0.7	0.26	<.83	39
2	0.19	0.02	0.33	<.040	0.2	0.07	<.030	1.6	<.040	0.39	0.17	<.83	32
3	<.040	<.030	<.060	<.040	<.11	<.12	<.030	<.020	<.040	<.060	<.23	<.83	<.050
4	<.040	<.030	<.060	<.040	<.11	<.12	<.030	0.03	<.040	<.060	<.23	<.83	<.050

Sample B	ALDRIN	A-BHC	B-BHC	G-BHC	PPDDD	PPDDT	HPTCL	DIELDRIN	ENDOII	ENDRIN	ENDALD	HPTCLE	NEMAGON
Inlet	0.05	<.036	<.071	<.048	0.19	<.14	0.03	0.35	0.51	0.19	<.23	0.06	<.060
1	<.040	<.030	<.060	<.040	0.08	<.12	<.030	0.08	<.040	0.13	<.23	<.83	<.050
2	<.040	<.030	<.060	<.040	<.11	<.12	<.030	<.020	<.040	<.060	<.23	<.83	<.050
3	0.014	<.030	<.060	<.040	0.004	<.12	0.02	0.42	<.040	0.14	<.23	<.83	14
4	<.040	<.030	<.060	<.040	<.11	<.12	<.030	<.020	<.040	<.060	<.23	<.83	<.050

Sample C	ALDRIN	A-BHC	B-BHC	G-BHC	PPDDD	PPDDT	HPTCL	DIELDRIN	ENDOII	ENDRIN	ENDALD	HPTCLE	NEMAGON
Inlet	<.040	<.030	<.060	<.040	0.17	<.12	<.030	0.26	0.41	0.14	<.23	0.06	<.050
1	0.08	0.05	0.39	0.01	0.33	0.15	0.05	2.9	1.1	0.78	<.23	<.83	42
2	<.040	<.03	<.60	<.040	<.11	<.12	<.030	<.020	<.040	0.06	<.23	<.83	<.050
3	<.040	<.030	<.60	<.040	<.11	<.12	<.030	0.42	<.040	0.05	<.23	<.83	<.050
4	0.02	<.030	0.13	<.040	0.06	<.12	<.030	0.5	<.040	0.08	<.23	<.83	17

Volatiles (ug/L)

Sample A	CHCL3	TCE	BENZENE	CIBEN
Inlet	3500	210	44	2000
1	1300	15	84	170
2	990	<25	<25	92
3	750	<25	<25	<25
4	570	<25	<25	<25

Sample B	CHCL3	TCE	BENZENE	CIBEN
Inlet	1800	110	34	1100
1	1300	7.7	77	140
2	1000	<25	<25	54
3	750	<25	<25	<25
4	570	<25	<25	<25

Sample C	CHCL3	TCE	BENZENE	CIBEN
Inlet	1800	110	41	1300
1	1300	12	80	150
2	1000	<25	33	38
3	780	<25	<25	<25
4	590	<25	<25	<25

*BDL-below detection limit

System conditions at time samples taken

H2O2 ppm	CHEMetric	RQ Flex	ORP	Residual	O3 ppm
Inlet	250	278	106	Inlet	----
1	250	150	211	1	0.2
2	175	100	270	2	0.2
3	150	100	196	3	0.2
4	100	90	213	4	0.2

Flow	O3 gen %	pH In	pH Out
.86gpm	2.25	7.62	7.9

HNU readings

Influent Tank 15 ppm
Column 1 off-gas 35 ppm
Column 1 off-gas after GAC 0 ppm
Columns 2,3,4 off-gas 1 ppm
Columns 2,3,4 off-gas after GAC 0 ppm

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. AGENCY USE ONLY *(Leave blank)*	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED
	March 1998	Final report

4. TITLE AND SUBTITLE
A Pilot-Scale Assessment of Peroxone Oxidation for Potential Treatment of Three Contaminated Groundwaters at the Rocky Mountain Arsenal, Commerce City, Colorado

5. FUNDING NUMBERS

6. AUTHOR(S)
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7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
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3909 Halls Ferry Road, Vicksburg, MS 39180-6199

8. PERFORMING ORGANIZATION REPORT NUMBER
Technical Report
SERDP-98-7

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
U.S. Army Corps of Engineers, Washington, DC 20314-1000;
Office of Program Manager, Rocky Mountain Arsenal
Commerce City, CO 80022-2180

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES
Available from National Technical Information Service, 5285 Port Royal Road, Springfield, VA 22161.

12a. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for public release; distribution is unlimited

12b. DISTRIBUTION CODE

13. ABSTRACT *(Maximum 200 words)*

Peroxone technology is based on the combination of hydrogen peroxide (H_2O_2) and ozone (O_3) for the generation of the hydroxyl radical ($OH\cdot$), which is a powerful reactive species in water, to further oxidize the organic contaminants. The main objective of this study was to determine the technical feasibility of using a peroxone system for treatment of contaminated groundwaters at the Rocky Mountain Arsenal (RMA). Past military and industrial activities at RMA have resulted in the contamination of the alluvial aquifer with various organic compounds such as diisopropylmethyl-phosphonate (DIMP), pesticides, and volatile organic compounds. The U.S. Army Engineer Waterways Experiment Station (WES) has been tasked by the Department of Defense's (DoD) Office of Strategic Environmental Research and Development Program to investigate the potential of peroxone for treating contaminated groundwaters at DoD installations.

The peroxone oxidation pilot system used in this study was constructed and assembled by the WES Environmental Restoration Branch and the WES Directorate of Public Works. The unit consisted of four glass columns (6-ft diam and 14 ft in height) plumbed in series, a holding tank (500 gal) for influent water supply, two 3-lb-per-day ozone generators, a microcomputer for data logging, oxidizer injection systems, and monitors for vapor and aqueous phase concentrations of hydrogen peroxide and ozone.

(Continued)

14. SUBJECT TERMS			15. NUMBER OF PAGES
BTEX	Hydrogen peroxide	Peroxone oxidation pilot system	87
Chlorinated Aliphatics	Organic contaminants	Pesticides	16. PRICE CODE
DIMP	Ozone		

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
UNCLASSIFIED	UNCLASSIFIED		

13. (Concluded).

Esstentially three independent pilot studies were performed during this effort. The three test influents were Influent of the North Boundary Containment System (NBCS), Well 213311 of the Basin A Neck System, and a composite sample (50/50) of Wells 01061 and 36001. The 50/50 composite was selected because the final concentration of the composite was considered characteristically similar to groundwater found within the Basin A and South Plant areas. Several oxidizer mass ratios (H_2O_2/O_3) and hydraulic residence times (HRTs) were studied.

The results of this study indicate that peroxone was effective for removing targeted contaminants from the NBCS influent and South Plant groundwater. The 250-mg/ℓ hydrogen peroxide, 2-percent ozone-dosed, and HRTs between 60 and 80 min were characteristics considered to be the optimal operating conditions for treating these two contaminated waters. Peroxone was considered ineffective for treatment of the Basin A Neck system groundwater. The chemical matrix was considered too high in terms of contaminant levels and oxidizer scavengers present. Peroxone appears to be a viable process for removing organic contaminants from groundwaters. The effectiveness is dependent on water chemical matrix and contaminant level.